THE

LONDON, EDINBURGH, AND DUBLIN

# PHILOSOPHICAL MAGAZINE

AND

# JOURNAL OF SCIENCE.

[SIXTH SERIES.]

*NOVEMBER* 1925.

## XCIX. *Scattering of α-particles by Atomic Nuclei and the Law of Force.*

*By* Prof. Sir E. RUTHERFORD, *O.M., F.R.S., Cavendish Professor of Experimental Physics, and* J. CHADWICK, *Ph.D., Fellow of Gonville and Caius College, Cambridge* *.

IT is well known that the study of the "single" scattering of α-particles by atoms affords a powerful method for throwing light on the magnitude and nature of the forces close to the atomic nucleus. In the present paper, an account is given of numerous experiments that have been made on the scattering of α-particles by a number of elements, but particularly by light elements like aluminium and magnesium, which are disintegrated by α-particles with the emission of protons, and by a heavy element like uranium, which suffers spontaneous disintegration. It was hoped in this way to obtain evidence not only of the dimensions of these nuclei, but also of the variation of the law of force either near to the nucleus or actually within its structure, and thus to gain information as to the actual way in which nuclei are built up of their component protons and electrons.

In 1913, an elaborate series of experiments on the scattering of α-particles was made by Geiger and Marsden † in order to test the correctness of the nuclear theory of atomic structure. An α-ray tube filled with radon was used as a source of complex α-rays and the variation in number of α-particles

* Communicated by the Authors.

† Geiger and Marsden, Phil. Mag. xxv. p. 604 (1913).

scattered by thin metallic foils was examined for silver and gold over a range of scattering angle between 5° and 150°. The variation of number with the angle of scattering was in good accord with the theory over the whole range, indicating that the law of inverse squares was valid for the region between the nucleus and the K-ring of electrons. For an inverse square law, the number of particles scattered through a given angle should vary as the inverse fourth power of velocity of the $\alpha$-particles, and this was verified by direct experiment.

The maximum range of the $\alpha$-particles from the emanation tube was probably about 4 cm., and it can be calculated that the direct distance of approach of the $\alpha$-particle for a deflexion of 150° was $7{\cdot}5 \times 10^{-12}$ cm. for the silver nucleus and $4{\cdot}6 \times 10^{-12}$ cm. for the gold nucleus. Even for these short distances, the law of inverse squares appeared to apply, at any rate approximately, indicating that the radius of the nuclei must be very small.

The experimental arrangement was not suited to give an accurate measure of the nuclear charge itself. By the use of a modified method, in which the fraction of the number of $\alpha$-particles scattered through about 30° was accurately measured, Chadwick * found directly that the nuclear charge was equal to the atomic number of the element as defined by Moseley.

While the law of inverse square was thus shown to be valid for the heavier elements, the experiments of Rutherford † and Chadwick and Bieler ‡ showed that in the case of close collisions between $\alpha$-particles and hydrogen nuclei, where the closest distance of approach must be of the order $4 \times 10^{-13}$ cm., the law completely broke down. Not only was the number of hydrogen nuclei set in swift motion much greater than was to be expected on the point charge theory, but the variation of the number with velocity was entirely different.

In order to carry the question further, Bieler § made a study of the scattering of the light elements magnesium and aluminium for angles of scattering between 20° and 100°. The scattering of thin foils of these elements was directly compared with that of a gold foil for the same range of angle. Assuming that the scattering in the case of gold is in accord

* Chadwick, Phil. Mag. xl. p. 734 (1920).
† Rutherford, Phil Mag. xxxvii. p. 537 (1919).
‡ Chadwick and Bieler, Phil. Mag. xlii. p. 923 (1921).
§ Bieler, Proc. Roy. Soc. A, cv. p. 434 (1924).

with the inverse square law under the experimental conditions, any failure in the law of inverse squares for aluminium and magnesium would be clearly shown. Bieler found that the scattering of α-particles was less than the theoretical for both these elements, and that the difference was the more marked the swifter the α-particle. These results show that the law of inverse squares does not hold for these elements for close collisions with an α-particle. He found that the departure from the simple law could be accounted for by supposing that the force between an α-particle and the nucleus was due to the combination of a law of repulsion according to the inverse square and a law of attraction varying as the inverse fourth power.

In interpreting these experiments, it has to be borne in mind that some of the collisions with aluminium and magnesium nuclei give rise to the emission of protons. Without special experiments, it is difficult to estimate the influence of these disintegrations on the amount of scattering, but, from the experiments considered later, it is probable that the correction is small.

In the light of these conclusions, it became of importance to re-examine the question whether the law of the inverse square holds accurately for the closest possible distance of approach for the heavy elements and to determine as accurately as possible the variation of scattering with velocity of the α-particle for the lighter elements.

A special interest attaches to a close examination of the law of scattering for the element uranium. If we assume that the α-particle emitted during the transformation of uranium acquires all its energy in escaping from the repulsive field of the nucleus, it can at once be calculated that the radius of the nucleus cannot be less than $7 \times 10^{-12}$ cm. If the α-particle has some initial velocity, the estimate of the radius is still higher. On this view, an α-particle of range equal to that emitted by uranium, viz. 2·7 cm., fired directly at the nucleus must enter its structure, while an α-particle from radium C of range 7 cm. must penetrate deeply into the nuclear region. On these views, we should anticipate that the law of inverse squares should no longer hold for close collision of a swift α-particle with the uranium nucleus.

In the case of the light elements like aluminium, which emit protons under α-particle bombardment, it is of great importance to settle what fraction of the close collisions leads to the emission of a proton. It is also important to examine whether any evidence can be obtained as to the fate of the

$\alpha$-particle in a disintegrating collision. Recently Blackett * has obtained evidence by Wilson photographs that in the case of nitrogen the $\alpha$-particle is captured when a proton is expelled. In order to throw light on this question we have made a careful examination of the distribution with velocity in the scattered $\alpha$-particles from all the elements examined.

### *Statement of the Problem.*

In the experiments to be described in this paper we are concerned with the interactions of an atomic nucleus and an $\alpha$-particle in close collision. In many cases of such collisions the distance between the two particles may be so small that it may not be permissible to assume either particle to behave as a point charge or to assume that the law of force is that of the inverse square. In general, all that can be done experimentally is to direct a beam of $\alpha$-particles on to the nucleus and to count the numbers of $\alpha$-particles scattered in various directions. If we assume that both momentum and energy are conserved in the translational motion of the particles, then the experiments can be made to lead to a relation between three variables, V the initial velocity of the $\alpha$-particle, $\phi$ the angle of scattering, and $n$ the fraction of $\alpha$-particles scattered through more than $\phi$. This relation has been called by Darwin † the collision relation. The fraction $n$ is a measure of the probability of a collision resulting in a deflexion of the $\alpha$-particle through an angle greater than $\phi$, and the probability of such a collision will of course depend on the forces between the particles and on their structure. The interpretation of the experiments will consist in devising some structure of the particles and some field of force which will give the observed relation between $n$, V, and $\phi$.

The validity of the assumption that energy is conserved in translational motion in these close collisions can be tested by measuring the velocity of the $\alpha$-particle scattered at a definite angle. This is, however, a point which it is difficult to test with precision, though a rough check can be readily obtained. It seems probable that in most collisions the conservation of energy holds, but there are cases where we know already that it fails, *e. g.* protons can be ejected from the aluminium nucleus which have more energy than the incident $\alpha$-particle, and in the bombardment of heavy nuclei, such as gold, by $\alpha$-particles, a very small but definite amount

* Blackett, Proc. Roy. Soc. A, cvii. p. 349 (1925).
† Darwin, Phil. Mag. xli. p. 486 (1921).

of γ-radiation is emitted. In these cases, the experiments must be described by a more complicated relation involving further variables. In collisions where the nucleus is disintegrated it would be necessary to count the numbers of protons emitted in various directions for a known beam of α-particles, and to measure their velocities.

It is evident then that if experiment should reveal a departure from the collision relation given by point charges and an inverse square law of force it would be necessary to carry out a very detailed series of observations before definite conclusions could be drawn about the structure of nuclei and the forces around them. If, in addition, many of the collisions are anomalous, that is, the conservation of energy does not hold, the problem becomes still more complicated, and it may be difficult or even impossible to collect experimentally the information which is necessary for the solution.

We have not as yet been able to carry out scattering experiments in such detail as to afford a fairly complete picture of the collision relation in any particular case, but we have examined under suitable conditions several elements, concentrating our attention on the search for a departure from the usual laws of scattering.

These laws, obtained on the assumption that the particles can be regarded as point charges, may be briefly stated. Let E, M, V be the charge, mass, and velocity of the incident α-particle, $m$, $Ze$ the mass and charge of the nucleus. After collision let the nucleus travel at an angle $\theta$ and the α-particle at an angle $\phi$ with the initial direction of motion of the α-particle. If momentum and energy are conserved in the collision we find

$$\tan\theta = \frac{m\cot\phi + \sqrt{m^2\,\mathrm{cosec}^2\phi - \mathrm{M}^2}}{\mathrm{M}+m}$$

if $m > \mathrm{M}$, as is generally the case; and the velocity of the α-particle after the collision is given by

$$v = \frac{\mathrm{V}}{\mathrm{M}+m}\left[\mathrm{M}\cos\phi + \sqrt{m^2 - \mathrm{M}^2\sin^2\phi}\right].$$

Assuming that the law of force between the particles is that of the inverse square, then, if $p$ be the length of the perpendicular from the nucleus to the initial line of motion of the α-particle,

$$p = \mu\tan\theta$$

where

$$\mu = \frac{Ze\mathrm{E}}{\mathrm{V}^2}\left(\frac{1}{\mathrm{M}}+\frac{1}{m}\right).$$

The orbit of the $\alpha$-particle is an hyperbola, and the distance of closest approach to the nucleus is given by

$$D = \mu\ (1 + \sec\theta).$$

The fraction $n$ of $\alpha$-particles scattered through an angle greater than $\phi$ by a foil of very small thickness $t$ and containing N scattering nuclei per c.c. will be

$$n = \pi p^2 N t$$
$$= \pi N \mu^2 \tan^2 \theta.$$

It is of course at large angles of scattering, that is, for small values of $\theta$, that we should expect to find a divergence from the above relations, if any exists. In the chief series of experiments described in this paper the average angle of scattering was 135°. This is the largest angle of scattering that is practically convenient, and the $\alpha$-particle under such conditions approaches the nucleus within ·96 of the closest distance possible in a head-on collision. Experiments at such a large angle of scattering have another advantage inasmuch as any change of the law of force would show itself more clearly than for scattering at an oblique angle. A little consideration shows that a large part of the deflexion of the $\alpha$-particle occurs in a region near the apse of its orbit. This region is the more confined the larger the angle of scattering. It will be seen that such considerations are of especial importance in interpreting the data obtained from the experiments. Another series of experiments was carried out in which the scattering-angle was 90°.

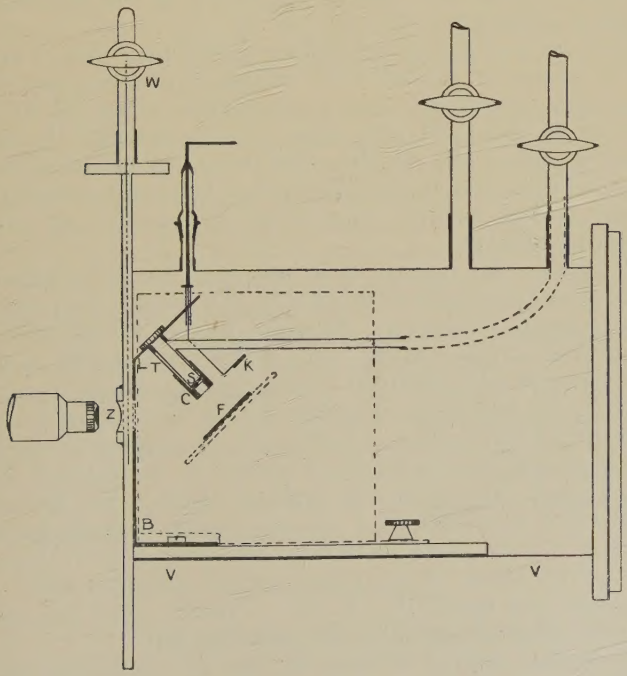
In both sets of experiments the scattering-angle was kept fixed and the velocity of the bombarding particles was varied by adding sheets of mica of known stopping power in the path of the rays. If the inverse square law held, the number $n$ of particles scattered by the foil should be proportional to $V^4$ where V is the velocity of the particles. Consequently $nV^4$ should be constant. By this method, any change in the law of force would at once be evident by comparison of the numbers of particles scattered at different speeds. A further check could be obtained by comparing the actual number scattered with that to be expected under the experimental conditions on the simple theory stated above. This quantitative comparison of experiment with theory could only be made approximately as it was not possible in the experimental arrangement to compare directly the numbers of bombarding and scattered particles by counting on the same screen (see Chadwick, *loc. cit.*). The apparatus, however, could be standardized by comparing

the scattering of an element with that shown by gold under identical conditions. It will be seen that special experiments by the direct method originally used by Chadwick showed that the scattering of gold was in close accord with the simple theory over the range examined.

*The Experimental Arrangement.*

The apparatus used in measuring the scattering of α-particles at an average angle of 135° is shown diagrammatically in fig. 1. The source, S, was carried on a brass

Fig. 1.




rod fitting into a narrow tube T, which was fixed in the brass plate BL, bent at L at an angle of 45°. The end of the tube T was covered with a thin sheet of collodion of about 3 mm. air equivalent. The diaphragm C served to limit the beam of α-particles and was made of graphite to reduce extraneous scattering. The α-particles then fell normally on F, a thin foil of the element under examination. This was carried on a rectangular graphite frame, which was placed in position on slides fixed to two

graphite plates (shown by dotted lines). The brass plate BL and the graphite sheets were fixed to a stout brass slide which fitted closely into the brass box V. The front face of this brass vessel consisted of a thin box in which a plate carrying absorbing screens of mica could be moved by means of a winch W. The zinc sulphide screen Z was fixed directly on the box. In the earlier experiments with a scattering-angle of 135°, the internal dimensions of the brass vessel were 2 cm. × 6 cm. × 17 cm. In later experiments a larger vessel was used, of internal dimensions 3 cm × 9 cm. × 20 cm.

The box was placed between the poles of an electromagnet in order to reduce the luminosity excited in the ZnS screen by the $\beta$-radiation.

The source of $\alpha$-rays was a brass or platinum disk of about 3 mm. diameter, coated with radium active deposit. The $\alpha$-particles, therefore, had a maximum range of 7 cm., reduced to about 6·7 mm. after passing through the fixed collodion film. By placing absorbing screens of mica or collodion immediately over the fixed collodion film, $\alpha$-particles of any desired smaller range could be obtained and their scattering observed.

There are two sources of error which must be guarded against in experiments of this kind. The first is the presence of extraneous scattering. To avoid this as far as possible, all surfaces exposed to the beam of $\alpha$-rays from the source were covered with sheets of pure graphite, except of course the foil, the scattering of which was to be measured. The scattering from carbon is small, and, on account of the low atomic weight, the $\alpha$-particles scattered at an angle of 135° have a range only ·17 of the incident range. For example, an incident $\alpha$-particle of 7 cm. range will be reduced to a range of 1·2 cm. after scattering by a carbon atom through 135°. The effect of scattering by the graphite-walls was measured very carefully. It was generally small compared with the effect of the foil under examination.

The second source of error is due to "contamination." When a bare source of active deposit is used in a vacuum it is invariably found that surfaces close to it gain a small activity. This activity may be due partly to recoil from traces of radium A still on the source, or to a small amount of emanation absorbed in the source, or perhaps to some volatilization or mechanical removal of the active matter. Even a very small contamination is sufficient to ruin such experiments as these, where we are observing an extremely minute fraction of the total number of $\alpha$-particles emitted by

the source. To guard against such error, the source was enclosed in the tube T, and this tube was evacuated by separate leads from those used for evacuating the main vessel. In this way the recoil of any active material or its diffusion into the vessel V was prevented. In addition a slow stream of oxygen was circulated through the box, being led in through the tap W, so that the flow was away from the ZnS screen towards the back of the box. This would minimise the effect of traces of emanation which might diffuse through the thin collodion film on tube T. The pressure of the oxygen in the box was from 1 to 2 mm. of mercury. Even with these precautions we generally found a slight contamination of about three or four particles per minute. At any point of an experiment the contamination effect could be measured by turning the graphite screen K so as to close the opening of the diaphragm C.

The general procedure observed in an experiment was as follows :—The source of active deposit was first measured by comparison of its $\gamma$-ray activity and placed in position about 20 minutes after removal from the emanation. This interval gives time for the radium A to decay to a small fraction of its initial amount. A disk of mica of air equivalent such as to reduce the range of the $\alpha$-particles to the required value was placed over the collodion film. A dummy carbon frame, *i. e.* without a scattering foil, was placed in position and the carbon effect was measured for different absorptions in the path of the scattered particles. The scattering-foil was then placed on the frame, and the total scattered particles were counted. At intervals during the measurements the incident $\alpha$-particles were cut off by means of the screen K. The effect then observed was due to contamination and to the natural effect of the ZnS screen.

### *Experiments at* 135°.

In the earlier experiments at 135° the distance from the scattering-foil to the ZnS screen was 41 mm. In the later experiments this distance was reduced to 34 mm. In both cases the distance from the source to the foil was about 14 mm. In the cases of the heavy elements, the scattering-foil had an area about 8 mm. $\times$ 8 mm., and a thickness corresponding to an air equivalent of about 2 mm. The scattering of the lighter elements was so small that a larger area and greater thickness of foil had to be used. In no case, however, was the air equivalent of the scattering-foil greater than 5 mm.

The results of our observations of scattering by most of the elements investigated may be stated very briefly. Within the accuracy of experiment we could find no divergence

Fig. 2.

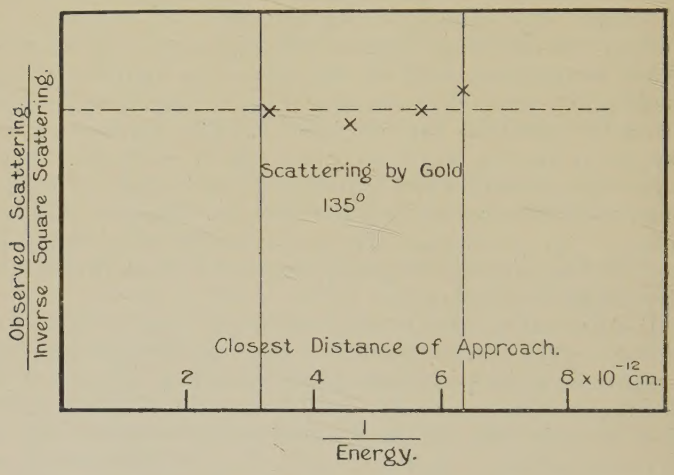
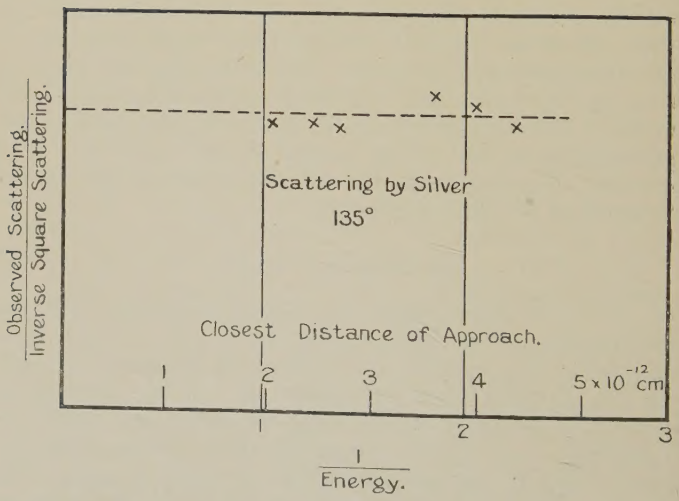



Fig. 3.




from the simple laws of scattering in the cases of gold, platinum, silver, and copper. The variation of the scattering by gold and by silver with the velocity of the $\alpha$-particle is shown in figs. 2 and 3, where the fraction of $\alpha$-particles

scattered is plotted against the reciprocal of the energy of the α-particle. The closest distance of approach of an α-particle to the nucleus is, for a given angle of scattering, inversely proportional to the energy of the particle. The abscissæ therefore represent also the region around the nucleus which has been investigated, and a scale of distances is given in the figures. The dotted line gives the amount of scattering to be expected on the simple theory. It will be seen that there is no evidence of any departure from the theory, either in the variation of scattering with velocity of the α-particle or in the actual fraction of particles scattered, within the limits of error of the experiments, about 10 per cent. The calculation of the absolute value of the scattered beam can only be made approximately, for the distances involved in the calculation are small and difficult to measure with accuracy, and in addition the efficiency of the ZnS screen has to be measured by a separate experiment. We have assumed here that the scattering of gold is normal and other elements are compared against gold as standard. It will be seen later that this assumption is confirmed by accurate experiments.

It should be mentioned that the experiments on the scattering of α-particles of short range, say below 3 cm., are subject to an error due to the "straggling" of the incident beam of particles. At these low ranges the average velocity of the particles can only be estimated approximately, and with ranges of less than 2 cm. the error becomes very serious, for it must be borne in mind that the scattering increases as the fourth power of the velocity of the particles.

The distribution of velocity of the α-particles in the scattered beam was tested by counting the number of scintillations observed when sheets of mica of various stopping powers were introduced on the slide just in front of the ZnS screen. The result of such an experiment is shown in fig. 4 In this experiment the scattering-foil was of gold and had a stopping power of 2 mm. of air, while the range of the incident α-particle was 6·7 cm. The foil was larger than that usually used, and the angle of scattering of the α-particles reaching the ZnS screen varied from 120° to 150°. On the assumption that energy and momentum are conserved in the collision, the ranges of the scattered particles should vary from 5·5 to 6·1 cm., under our experimental conditions. We should expect the absorption curve for such a beam of particles to remain constant up to an absorption of about 4·5 cm. and then to decrease steadily to zero at 6·1 cm. The curve shows that this is confirmed by experiment as closely as such measurements allow.

As far as these experiments go, there is no evidence that the simple laws of scattering fail to hold for the elements gold, platinum, silver, and copper. The fraction of $\alpha$-particles scattered by these elements at an average angle of 135° varies inversely as the square of the energy of the incident particles, and the ranges of the scattered particles agree with those calculated from theory.

Fig. 4.

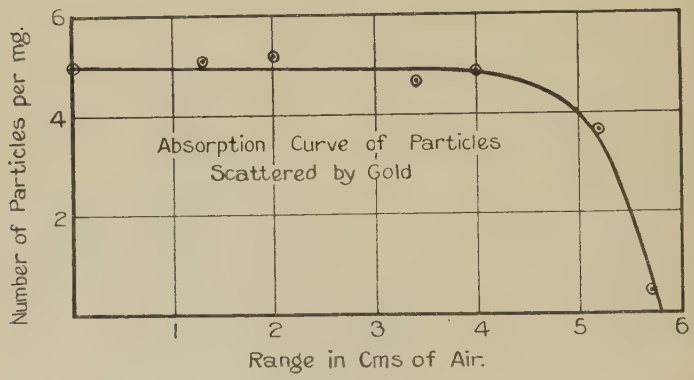
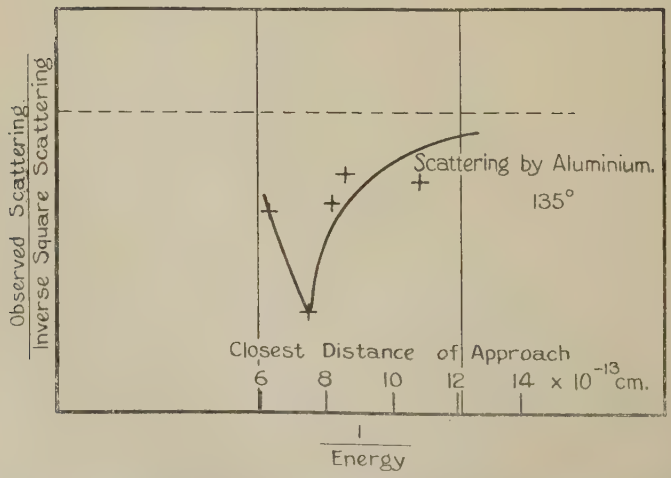


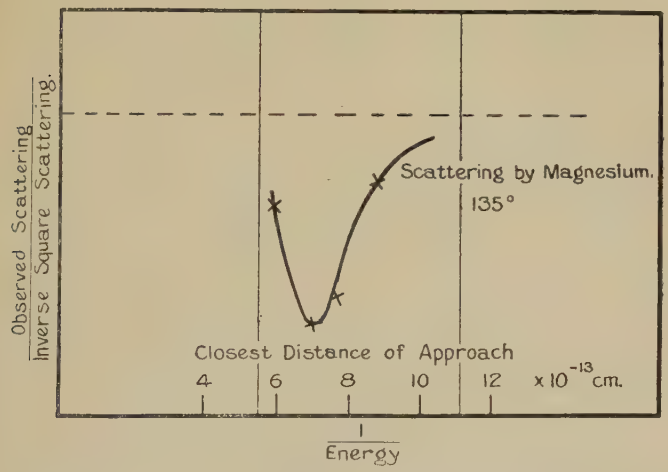

Fig. 5.




Experiments were also made on the scattering of two light elements, magnesium and aluminium, and here a very striking departure from the usual laws of scattering was observed. This will be seen from figs. 5 and 6, where, as

before, the number of α-particles in the scattered beam is plotted against the reciprocal of the energy of the incident α-particle. The dotted line gives the number to be expected on the simple theory.

Fig. 6.



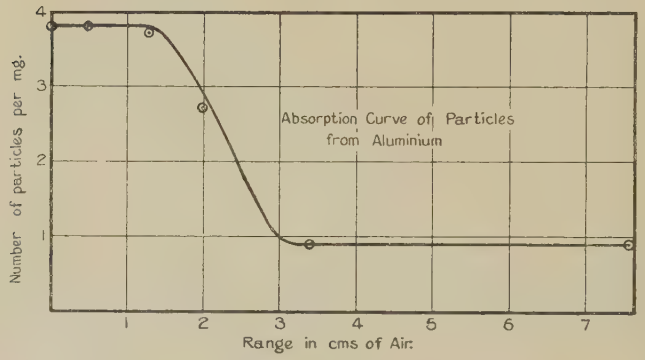

The scattering of α-particles of 6·7 cm. range was less than the theoretical, and *decreased* as the energy of the incident α-particles was diminished, falling to a minimum for particles of range about 5 cm. The scattering then increases again and approaches the theoretical value for particles of small range. This is a most unexpected result, and a very large number of experiments has been made to confirm it. The observations are difficult on account of the small scattering from aluminium and magnesium, and also on account of the small range of the scattered particles. The scattering from the carbon shields thus becomes important, and in addition H-particles are present, due to disintegration of some nuclei in the collisions. When the range of the incident α-particle is small the scattered beam, on account of the "straggling" and of absorption in the scattering-foil, consists of particles of a wide range of velocity, and the counting is not so accurate.

In a special series of experiments on aluminium the change in the number of scattered particles was observed when the incident range was changed from 6·8 to 5·3 cm., other conditions remaining the same. About 1000 particles were counted at each point. The results showed definitely that

the scattering of $\alpha$-particles of 5·3 cm. range was less than the scattering of those of 6·8 cm. range, while on the usual theory it should have been 40 per cent. greater.

The absorption curve of the particles scattered from aluminium is given in fig. 7. The range of the incident $\alpha$-particles was 6·7 cm. and the air equivalent of the scattering-foil was 5 mm. The small number of particles which

Fig. 7.




still remain at an absorption of 3·4 cm. are protons arising from the disintegration of the aluminium nucleus. This curve will be discussed later.

*Experiments at* 90°.

In order to obtain a check on the measurements of the scattering at 135° recorded above, a further series of experiments was carried out in which the scattering-angle was 90°. The experimental arrangement is shown in fig. 8. Except for the geometrical changes necessitated by the change in the scattering-angle, the arrangement is the same as that used in the previous experiments. The distance from the source to the centre of the scattering-foil was 15 mm., and from the centre of the foil to the screen 34 mm. The dimensions of the foil were 14 mm. × 14 mm.

The results obtained for magnesium and aluminium are shown in figs. 9 and 10. In both cases the foils were of about 5 mm. air equivalent. The dotted line gives the theoretical value of the scattering, deduced from measurements of the scattering of a thin gold-foil under the same conditions. The curves show that the amount of scattering of both magnetism and aluminium decreases rapidly as the range of the $\alpha$-particle increases from 4 to 6·7 cm. For a

Fig. 8.

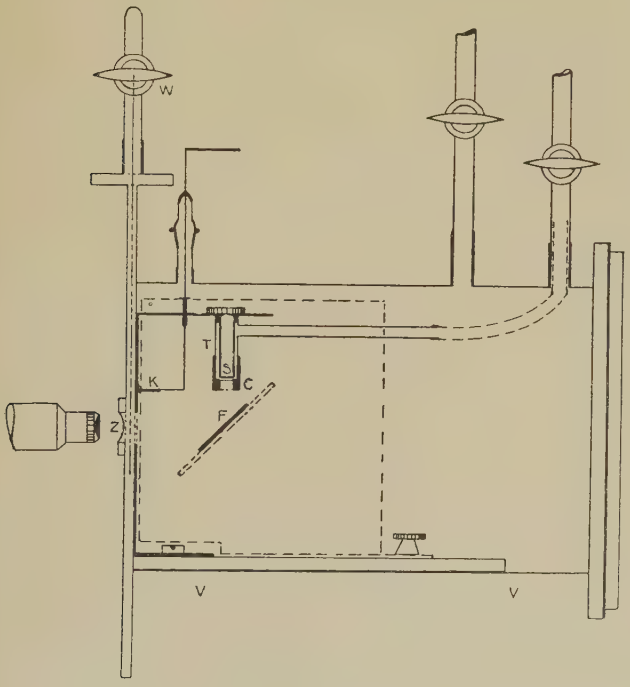
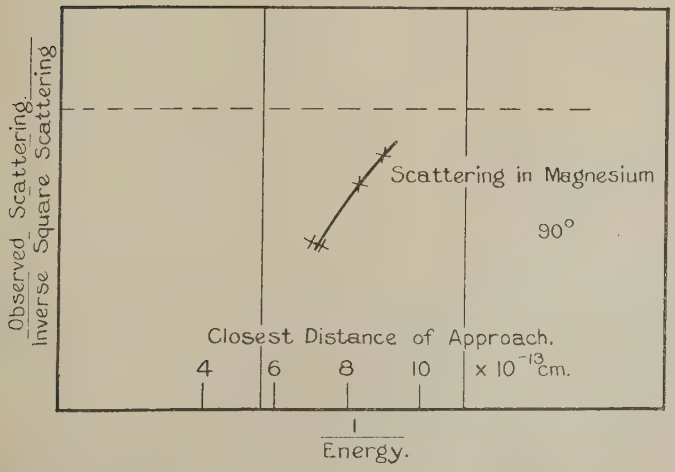
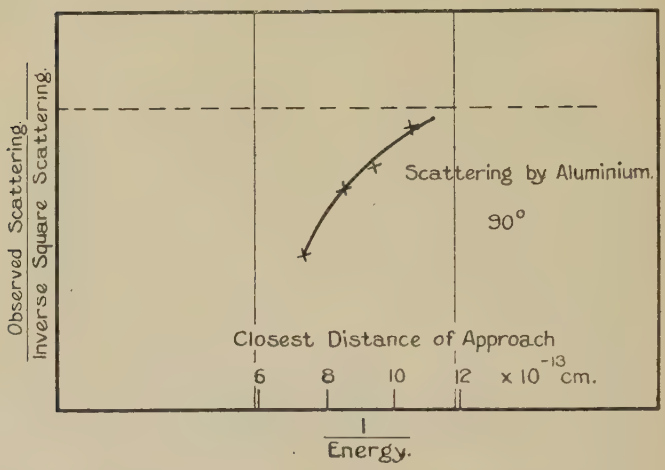

W
T
S
K
C
F
Z
V
V

Fig. 9.


Observed Scattering / Inverse Square Scattering
Scattering in Magnesium
90°
Closest Distance of Approach.
4
6
8
10
x 10⁻¹³ cm.
1 / Energy.

particle of 4 cm. range the scattering agrees approximately with the theoretical value, while for a particle of 6·7 cm. range the scattering is about half the theoretical. When we

Fig. 10.




take into account the change in the scattering-angle and the consequent change in the apsidal distance of collision these results confirm those obtained at an angle of 135°.

*Experiments on the Scattering by Uranium and Gold.*

We have pointed out earlier in this paper that a special interest is attached to the examination of the scattering of uranium, for it seems certain that a fast $\alpha$-particle in close collision must penetrate the nuclear structure of the uranium atom. We have therefore examined the scattering from a thin film of uranium at an angle of 135° by the method described above. The film of uranium was prepared by cathode sputtering, using a piece of metallic uranium, and was deposited on a plate of graphite 1 sq. cm. in area *. The amount of uranium in the film was measured by counting the number of $\alpha$-particles emitted, and also by comparing its activity in an electroscope with that of a thin deposit of uranium oxide. The thickness of the film measured in this way corresponded to an air equivalent of about 2 mm. and to a weight of 1 mg. per sq. cm. The amount of uranium on

* The rate of sputtering was very slow compared with other heavy metals, and a film on a glass surface was surprisingly transparent.

such an area of the film is too small to be measured with any accuracy.

The scattering of this film of uranium was compared with that of gold under the same conditions. Within the error of our experiments the scattering was parallel to that of gold, and there was no indication of a departure from the usual laws, even when the incident α-particles had as short a range as 2 to 3 cm. Experiments with α-particles of such short range are, however, very difficult to carry out accurately on account of the large "straggling" and the consequent indefiniteness in the average range of the incident α-particles. The numbers of scattered particles were about those to be expected from the estimated thickness of the film, but, as we have mentioned, the latter is difficult to determine with the necessary precision. The ranges of the particles scattered from uranium were also examined with care, but there was no evidence that the ranges did not agree with the theoretical values.

The experiments previously described have shown that the scattering of gold varies with the velocity of the incident α-particles in the manner demanded by inverse square forces. Before we can say definitely that the scattering of gold is normal, it remains to be shown that the actual amount of scattering for the distances of collision agrees with the calculated value; in other words, that the nuclear charge of gold deduced from scattering experiments corresponds to its atomic number. To determine this point, we adopted the method used by Chadwick for the measurement of nuclear charges. This method has the advantages that both the scattered and direct beams are counted on the same ZnS screen, thus eliminating the necessity for determining the efficiency of the screen, and that the geometrical conditions can be made so definite that the accuracy of experiment depends mainly on the probability error in counting the α-particles. For a description of the arrangement and the method of experiment the reader must be referred to Chadwick's paper. The arrangement we used was very similar to his, the chief difference being that in our experiments the angles of scattering were much greater, to correspond to the distances of collision involved in the experiments at 135°.

In the first set of experiments the range of scattering-angle was from 40° to 70°, and the scattering was measured for α-particles of 6·7 cm. incident range, and also of 4·4 cm. range. The observations with the latter particles gave a check against Chadwick's measurements, where the scattering-angle was from 20° to 35° and the α-particles had an

average range of 6·6 cm. The results, interpreted on the simple theory, gave a nuclear charge for gold less than 2 per cent. from the atomic number, and comparison of the amount of scattering of particles of different ranges showed that the inverse square law of force held very closely.

A similar series of experiments was carried out in which the scattering-angle varied from 65° to 100°. The same result was found, that the scattering was normal to within about 2 per cent.

These results show that the gold nucleus behaves as a point charge and that the law of force is the inverse square for distances of approach corresponding to scattering-angles from 20° to 100°, that is, for distances from $10 \times 10^{-12}$ to $3{\cdot}5 \times 10^{-12}$ cm. from the nucleus. These distances correspond to a scattering at 135° of particles of 1 25 cm. range and 6 cm. range respectively. The experiments at this angle showed that the scattering obeyed the law of inverse square for particles of ranges from 6·7 to 2·4 cm. We may therefore safely conclude that within the error of experiment the scattering of gold is normal over the whole range examined. This means that the gold nucleus behaves as a point charge of $79e$ for distances of approach between $3{\cdot}2 \times 10^{-12}$ and $10^{-11}$ cm.

Special attention was paid to the scattering of uranium and gold for distances of approach about 6 to $8 \times 10^{-12}$ cm. for the following reasons. In the case of uranium it seems clear that some parts of the nuclear structure extend to a radial distance of about $7 \times 10^{-12}$ cm., and the general radioactive evidence suggests that the nucleus may consist of a central charged core surrounded by a number of satellites. In our experiments on scattering at 135° the $\alpha$-particle approaches to a distance of $7 \times 10^{-12}$ cm. from the uranium nucleus when it has a range of 2·9 cm. It is unfortunately very difficult to make accurate observations at such low ranges on account of the straggling of the $\alpha$-particle beam, and we were unable to find any divergence from the normal scattering in this region. Owing to the difficulty in measuring the thickness of the uranium film we could not determine the absolute magnitude of the scattering of fast $\alpha$-particles with any precision, but our results indicate that the scattering of 6·7 cm. particles is normal to within about 20 per cent. This would show that the charge on that part of the uranium nucleus which lies within a distance of about $4 \times 10^{-12}$ cm. of the centre was within 10 per cent. of the normal nuclear charge.

It is reasonable to suppose that a heavy nucleus like gold

has a similar structure to that of uranium, and therefore that some change in the law of scattering might be expected for a distance of collision of about $7 \times 10^{-12}$ cm. In the case of gold the experiments can be carried out with precision by the annular ring method, suitable angles of scattering being selected. Our results, however, afford no evidence of any change in the law of scattering in this region. It seems clear then, that if satellites are present in the gold nucleus, both positive and negative satellites must be present and of about equal total charge, and that the charge on the central core must be very nearly the same as the total nuclear charge.

It is obviously of great importance that the scattering by uranium and other heavy elements should be examined with the greatest possible precision to see if any light can be thrown on the outer structure of the nucleus.

*The Ranges of the Particles scattered by Aluminium.*

Before discussing the interpretation of the peculiar scattering curves shown by magnesium and aluminium it is important to compare the experimental absorption curve of the scattered particles, given in fig. 7, with that to be expected for elastic collisions between the α-particle and the aluminium nucleus. In this experiment the incident α-particles had a range of 6·7 cm. and fell normally on a foil of aluminium of 5 mm. stopping power. The scattering-angle varied between 120° and 150°. Assuming that both momentum and energy are conserved in the collision, the ranges of the particles in the scattered beam should vary between 1·8 cm. for particles scattered at 150° from the back of the foil, and 3·3 cm. for those scattered from the front. The absorption curve of fig. 7 shows that the ranges of the scattered particles are in fair agreement with these calculations. The particles observed at ranges greater than 3·4 cm. are protons liberated by disintegration of the aluminium nucleus. Their number did not alter appreciably when the absorption was increased to 7 cm.

The results show no evidence of any appreciable number of α-particles of short range. This point has been examined with great care, for there was always the possibility that the α-particles observed might be due, at least in part, not to ordinary scattering but to a type of temporary radioactivity of the nucleus brought about by the intense collisions and resulting in the expulsion of α-particles. Under such conditions we should not expect the ranges of the escaping

particles to have the same distribution as for normal scattering. It should, however, be pointed out that some $\alpha$-particles of short range are always present under the experimental conditions, due to scattering from the carbon shields. These have, of course, been deducted from the total effect, but their presence complicates the observations and renders them less conclusive.

There was also the further possibility that this absorption curve would afford some evidence about the fate of the $\alpha$-particle which succeeds in ejecting a proton from the aluminium nucleus, for it seems very probable that an $\alpha$-particle which has been scattered through 135° must have penetrated into the critical region of the nucleus. The evidence is entirely negative, and, so far as it goes, is in favour of the capture of the $\alpha$-particle by the nucleus, in agreement with Blackett's direct observations on the disintegration of nitrogen. Some information might be derived from a comparison of the total number of $\alpha$-particles scattered at large angles and the total number of ejected protons, but the experimental results are at present too meagre to enable us to draw any definite conclusions. The number of protons observed from aluminium for $\alpha$-particles of 6·6 cm. range was about one-quarter of the number of scattered $\alpha$-particles. The number rapidly becomes less with decrease of velocity of the $\alpha$-particles and is very small for particles of range less than 5 cm. We are at present not in a position to estimate what fraction of the collisions of a given type result in a disintegration. Before this can be done, we require a detailed knowledge of the scattering-curve of the $\alpha$-particles and of the distribution of the protons as regards both direction and velocity. We hope to investigate this question later.

### *Minimum Velocity of Escape of Protons.*

In some experiments made last year * we mentioned that the protons liberated from aluminium had a minimum range of 13 to 14 cm. of air, and those from sulphur of 15 to 16 cm. In these experiments thin films of these elements were used, and the number of protons was observed in a direction at right-angles to the incident $\alpha$-particles of 7 cm. range. No appreciable change in the number of protons was noted when the stopping power of the absorbing screens in the path of the protons was increased from 7 to 13 cm. in the case

* Rutherford and Chadwick, Proc. Phys. Soc. Lond. xxxvi. p. 417 (1924).

of aluminium, and from 7 to 15 cm. in the case of sulphur. In the present experiments at an angle of 135° with the direction of the α-ray beam, no certain change in the number of protons from a thin foil of aluminium could be observed for absorptions between 3·4 and 7 cm. of air. In the case of aluminium we have thus shown that no change in the number of protons is observed for absorptions between 3·4 and 13 cm. of air. We have already pointed out that such a result suggests that the protons have their origin in a region where the potential due to the nucleus is about 3 million volts. Even if a proton is freed from this region with little or no velocity, it must acquire a minimum critical speed in escaping from the nucleus. This critical speed is about $2{\cdot}4 \times 10^9$ cm. per second.

It should be pointed out that while this critical speed of emission is on this view a property of the nucleus, the actual experimental observation of the minimum velocity may be affected to some extent by the motion of the nucleus due to the collision. We should anticipate that the minimum velocity would be somewhat greater in the forward than in the backward direction of the incident α-particles, from analogy with the difference in *maximum* range of the particles in these two directions.

### *Discussion of Scattering-Curves.*

We have seen that the scattering-curves for magnesium and aluminium vary in an unexpected way with the velocity of the α-particle, showing a minimum for particles of range about 5 cm. when the scattering-angle is 135°. In order to test whether the appearance of this minimum is connected with the nearness of approach of the α-particle to the nucleus, a series of experiments was carried out for a scattering-angle of 90°. A similar rapid decrease of the scattering with increasing velocity of the α-particle was observed, but this occurred at higher velocities of the α-particle than in the previous experiments. The presence of a corresponding minimum is very probable, but this could not be verified as it seems to occur for an average range of the α-particle of about 6·4 cm., the maximum which could be realized under our conditions of experiment and with a source of radium active deposit. The shift of the minimum is about that to be expected if the minimum of the curve in both cases corresponds to the same apsidal distance of the α particle. Assuming for simplicity of calculation that the law of inverse squares holds, the ratio of the ranges of the α-particles which

have the same apsidal distance for scattering at 90° and 135° is 1·16. The observed ratio is about 1·2.

Before considering a possible explanation of the scattering-curves, it is important to bear in mind the actual distances involved in these close collisions. Assuming the law of inverse squares, the apsidal distance for an $\alpha$-particle of 7 cm. range in a head-on collision with an aluminium nucleus is $5{\cdot}7 \times 10^{-13}$ cm. The corresponding distance for a 2 cm. particle is $13 \times 10^{-13}$ cm. These distances are very minute, being comparable with the dimensions of an electron or of an $\alpha$-particle. From their experiments on the collisions of $\alpha$-particles with hydrogen nuclei, Chadwick and Bieler concluded that the inverse square law held outside a spheroidal region round the $\alpha$-particle of semi-axes about $4 \times 10^{-13}$ cm. and $8 \times 10^{-13}$ cm. Inside this surface the forces increased very rapidly. It is seen that this estimate of the "dimensions" of an $\alpha$-particle, or rather of the region where the forces are abnormal, is of the same order as the distances involved in a close collision between an $\alpha$-particle and an aluminium or magnesium nucleus. If these views are correct, we can no longer assume that the forces between the colliding nuclei correspond to point charges, for we are dealing probably with the case of the interpenetration of two complex nuclear structures of similar dimensions. It is a matter worthy of remark that the distance for which the law of inverse squares obviously breaks down in aluminium and magnesium is about the same as that observed for a close collision between an $\alpha$-particle and a hydrogen nucleus. This may be a pure coincidence, but on the other hand it may indicate that the structure of the $\alpha$-particle is at least in part responsible for the abnormal scattering observed for aluminium and magnesium. Unfortunately, our knowledge of the structure either of the $\alpha$-particle or other nuclei or of the forces holding them together is too slight to give any definite answer to this question.

While the ordinary laws of collision have sufficed as yet in accounting for the scattering of $\alpha$- and $\beta$-particles, it is always well to bear in mind the possibility that in special cases scattering may in some way be governed by quantum conditions. For example, the amount of scattering at a particular angle may be affected if the angular momentum of the $\alpha$-particle round the nucleus $p\mathrm{M}\mathrm{V} = nh/2\pi$, where $n$ is a whole number. In the case of an $\alpha$-particle scattered through 135° by an aluminium nucleus, it can be calculated that $p\mathrm{M}\mathrm{V} = h/2\pi$ when $\mathrm{V} = 2{\cdot}3 \times 10^9$ cm. per sec. If $n = 2$, $\mathrm{V} = 1{\cdot}15 \times 10^9$ cm./sec. The corresponding ranges for

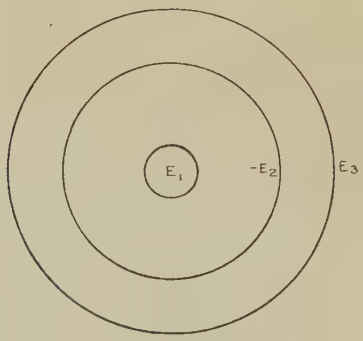
these velocities are 12·5 cm. and 1·6 cm. For scattering through 90°, the corresponding velocities are 5·6, 2·8, $1{\cdot}87 \times 10^9$ cm./sec. for $n=1$, 2, 3 respectively. The mean velocity between $n=1$ and $n=2$ for scattering through 135° corresponds to a range of 5·3 cm., in close accord with the range for which the scattering is a minimum. On the other hand, there is no agreement with experiment when similar assumptions are made for scattering at 90°. We may therefore conclude that the above agreement is fortuitous, and that the dip in the scattering-curve cannot be interpreted along such lines.

We have pointed out that Bieler tried to account for the departure of the scattering by aluminium and magnesium from the inverse square law by the assumption that the two nuclei concerned behaved as point charges, and that a force of attraction varying as the inverse fourth power of the distance was superimposed on the ordinary repulsion forces. Such a point of view was shown to account for the progressive departure from the normal scattering observed with increase of velocity of the α-particle. On such an assumption, however, it is difficult to account for the sudden increase of scattering which occurs for the swiftest α-particles, unless one supposes some other factors to come into play at these very small distances.

On looking at the scattering-curves for these two elements, an obvious general explanation suggests itself. Suppose for simplicity we assume that the α-particle may be regarded as a point charge, and that the abnormal scattering is to be ascribed to the complex structure of the aluminium or magnesium nucleus. This is the reverse of the assumption made in interpreting the collisions of α-particles with H-nuclei, where the complex structure is assigned to the α-particle. Suppose also that the aluminium nucleus is a complex system consisting of a charged central core surrounded by a satellite distribution of positive and negative charges. To illustrate the effects to be expected on the scattering, suppose the central core of charge E is surrounded at appropriate distances by a shell of charge $-E_2$, and outside this by a shell of charge $E_3$ (fig. 11). Outside this system the complex nucleus corresponds to a point charge $E = E_1 - E_2 + E_3$. Assuming that the law of inverse squares applies outside the the shell $E_3$ the α-particle is acted on by a central force from a charge E, between the shells $E_3$ and $E_2$ by a central force from the charge $E - E_3$, and between $E_2$ and $E_1$ by a central force from the charge $E + E_2 - E_3$. It is clear that outside the region $E_3$ the scattering will be normal. Inside

the shell $E_3$ there will be a sudden drop in the magnitude of the forces and inside the shell $E_2$ a sudden rise again. It can be shown by calculation that for particles which penetrate $E_3$ but not $E_2$ the scattering will be less than for a charge E, and will depart progressively from the normal as the edge of the shell $E_2$ is approached. The α-particle which is swift enough to enter $E_2$ comes at once under the action of a stronger field, and the scattering increases again.

Fig. 11.




It can be calculated that such a composite nucleus will give a variation in scattering very similar to that observed for the nucleus of aluminium or magnesium, provided we give suitable values to $E_2$ and $E_3$ and adjust the distance of the shells from the centre While recognizing that the assumptions made in this rough model cannot be realized in the actual structure of a nucleus, it is not improbable that the abnormal scattering of these nuclei may be due to a structure of the general type proposed. It has previously been pointed out that the radioactive evidence suggests a similar type of satellite structure for uranium and other radioactive elements. The failure to detect any abnormal scattering for uranium or for gold may indicate that the positive and negative charges of the satellites nearly balance each other. It may be that the satellites consist of charged doublets in which the charges are separated by a distance of the order of $3 \times 10^{-13}$ cm. A distribution of such neutral doublets would be difficult to detect in the case of uranium, but would be likely to show a pronounced effect on the scattering in aluminium and magnesium, where the distances involved in a collision are of about the same magnitude as the length of the doublet.

Before discussing the subject further, it is desirable to

have more precise information on the scattering of $\alpha$-particles by a number of the lighter elements, and particularly to know whether the scattering shows the same peculiarities in all. This will involve a large amount of careful work under difficult conditions.

In conclusion, some reference should be made to the fact that the minimum in the scattering-curve for aluminium occurs for about the same velocity of the $\alpha$-particle for which the liberation of protons is first observed. For example, we have shown that few protons could be detected from aluminium when the range of the $\alpha$-particle was less than 4·9 cm., while the dip of the scattering-curve occurs for particles of about the same range. The dip corresponds to a potential of about 3 million volts, and it has already been pointed out that the minimum velocity of escape of the protons from aluminium corresponds to about the same potential. These results suggest that protons are not liberated until the $\alpha$-particle actually penetrates the satellite system.

Our thanks are due to Mr. Osgood and Mr. Hirst for their assistance in counting, and to Mr. G. R. Crowe for his help in preparing the sources and arranging the experiments.

Cavendish Laboratory,
July, 1925.

---

C. *An Alternative Treatment of Fermat's Principle for a Stationary Gravitational Field.* *By* J. L. Synge *.

THE following treatment of Fermat's Principle is offered as an alternative to the proofs of Levi-Civita (*Nuovo Cimento*, vol. xvi. (1918) p. 105) and of Weyl ('Raum, Zeit, Materie,' 4th ed. p. 221). The former method is reproduced in Silberstein's 'Theory of Relativity,' 2nd ed. p. 380.

It will be seen that the following mode of proof does not require the use of the calculus of variations, except in the well-known fundamental theorem that if F be a function of coordinates $x_1, \ldots, x_N$ and their derivatives $\dot{x}_1, \ldots, \dot{x}_N$ with respect to a parameter $\lambda$, then the variational equation

$$\delta \int F d\lambda = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

* Communicated by Prof. J. Joly, F.R.S.

the end points and the terminal values of $\lambda$ being fixed, is equivalent to the Lagrangian equations

$$\frac{d}{d\lambda}\frac{\partial F}{\partial \dot{x}_r} - \frac{\partial F}{\partial x_r} = 0 \quad (r=1, \ldots, N). \quad . \quad . \quad . \quad (2)$$

In fact, (1) and (2) are alternative formulations of a single law; while (1) is more compact and for some purposes more suggestive, the form (2) is perhaps of a more precise nature.

The gravitational field under consideration is stationary; by this we understand that, if

$$ds^2 = g_{mn}\,dx_m\,dx_n \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

be the line element in space-time, $g_{mn}$ are all independent of $x_4$, the time coordinate. In what follows we shall use repeated Greek subscripts to denote summation from 1 to 3, Roman indices being reserved for summation from 1 to 4.

Fermat's Principle imposes two conditions on a light-path which passes through two events, A and B :—

(i.) The general propagation condition $ds=0$ is satisfied;

(ii.) $\int_A^B dx_4$ has a stationary value for the light-path when compared with neighbouring space-time curves which intersect the parametric lines of $x_4$ through A and B respectively (*i. e.* pass through the space-points $a$ and $b$ which are these parametric lines respectively) and also satisfy (i).

These conditions are expressible mathematically in the form :

$$\delta \int dx_4 = 0, \quad ds = 0, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or, in equivalent forms,

$$\delta \int \dot{x}_4\,d\lambda = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$2T \equiv g_{mn}\dot{x}_m\dot{x}_n = 0, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $\lambda$ is a parameter, chosen so as to have the same range of values for all the curves considered, and the point denotes differentiation with respect to it. T is defined by (6). Condition (6), which may also be written

$$2T \equiv g_{\mu\nu}\dot{x}_\mu\dot{x}_\nu + 2g_{\mu 4}\dot{x}_\mu\dot{x}_4 + g_{44}\dot{x}_4^2 = 0, \quad . \quad . \quad (7)$$

defines $\dot{x}_4$ as a function of $x_1, x_2, x_3, \dot{x}_1, \dot{x}_2, \dot{x}_3$. Thus (5) is a variational equation of the type (1), the manifold under consideration being the spatial manifold with coordinates

$x_1$, $x_2$, $x_3$; thus Fermat's Principle may be regarded as defining light-paths by the equations

$$\frac{d}{d\lambda}\frac{\partial \dot{x}_4}{\partial \dot{x}_\rho} - \frac{\partial \dot{x}_4}{\partial x_\rho} = 0, \quad (\rho = 1, 2, 3). \quad . \quad . \quad (8)$$

From (7) we find, by partial differentiation with respect to $\dot{x}_\rho$ and $x_\rho$ respectively, regarding $x_1$, $x_2$, $x_3$, $\dot{x}_1$, $\dot{x}_2$, $\dot{x}_3$ as the independent variables,

$$g_{\mu\rho}\dot{x}_\mu + g_{4\rho}\dot{x}_4 + (g_{\mu 4}\dot{x}_\mu + g_{44}\dot{x}_4)\frac{\partial \dot{x}_4}{\partial \dot{x}_\rho} = 0, \quad . \quad . \quad (9)$$

$$\frac{\partial \mathrm{T}}{\partial x_\rho} + (g_{\mu 4}\dot{x}_\mu + g_{44}\dot{x}_4)\frac{\partial \dot{x}_4}{\partial x_\rho} = 0, \quad . \quad . \quad (10)$$

where, in calculating $\partial \mathrm{T}/\partial x_\rho$, T is regarded as a function of $x_1, x_2, x_3, \dot{x}_1, \dot{x}_2, \dot{x}_3, \dot{x}_4$. Substituting from (9) and (10) in (8), and simplifying slightly by choosing $\lambda = x_4$, we obtain the equations of the Fermat light-paths in the form

$$\frac{d}{dx_4}\left(\frac{g_{\mu\rho}\dfrac{dx_\mu}{dx_4} + g_{4\rho}}{g_{\mu 4}\dfrac{dx_\mu}{dx_4} + g_{44}}\right) - \frac{\dfrac{\partial \mathrm{T}}{\partial x_\rho}}{g_{\mu 4}\dfrac{dx_\mu}{dx_4} + g_{44}} = 0, \quad (\rho = 1, 2, 3), \quad (11)$$

which define $x_1$, $x_2$, $x_3$ as functions of $x_4$.

Now in the General Theory of Relativity it is customary to define light-paths as geodesic null-lines. Since variations from a null-line lead to imaginary values of $ds$, it is desirable to define geodesics independently of the variational principle. The most convenient precise definition seems to be as follows:—*Any curve satisfying*

$$\ddot{x}_r + \left\{ \begin{matrix} m\ n \\ r \end{matrix} \right\} \dot{x}_m \dot{x}_n = 0, \quad (r = 1, 2, 3, 4), \quad . \quad . \quad (12)$$

*is a geodesic, the point denoting differentiation with respect to an independent variable* $\lambda$. The system (12) necessarily possesses the first integral,

$$2\mathrm{T} \equiv g_{mn}\dot{x}_m\dot{x}_n = \text{constant}. \quad . \quad . \quad . \quad . \quad (13)$$

We may define *particle-paths* as those geodesics for which T is *not zero*, and *light-paths* as those geodesics for which T is *zero*.

Equations (12) may also be exhibited in the covariant Lagrangian form:

$$\frac{d}{d\lambda}\frac{\partial \mathrm{T}}{\partial \dot{x}_r} - \frac{\partial \mathrm{T}}{\partial x_r} = 0, \quad (r = 1, 2, 3, 4). \quad . \quad . \quad (14)$$

The establishment of Fermat's Principle consists in proving that the solutions of the Fermat equations (11) are also solutions of (14). To show this we note that $\partial T/\partial x_4$ is zero, on account of the stationary character of the field, and therefore the last of equations (14) gives

$$\frac{\partial T}{\partial \dot{x}_4} \equiv g_{\mu 4}\dot{x}_\mu + g_{44}\dot{x}_4 = \text{constant}, \quad . \quad . \quad . \quad (15)$$

while the first three of (14) are

$$\frac{d}{d\lambda}\frac{\partial T}{\partial \dot{x}_\rho} - \frac{\partial T}{\partial x_\rho} = 0, \quad (\rho = 1, 2, 3), \quad . \quad . \quad . \quad (16)$$

or

$$\frac{d}{d\lambda}(g_{\mu\rho}\dot{x}_\mu + g_{4\rho}\dot{x}_4) - \frac{\partial T}{\partial x_\rho} = 0, \quad (\rho = 1, 2, 3). \quad . \quad (17)$$

Dividing (17) by (15), we obtain for the light-paths the equations

$$\frac{d}{d\lambda}\left(\frac{g_{\mu\rho}\dot{x}_\mu + g_{4\rho}\dot{x}_4}{g_{\mu 4}\dot{x}_\mu + g_{44}\dot{x}_4}\right) - \frac{\dfrac{\partial T}{\partial x_\rho}}{g_{\mu 4}\dot{x}_\mu + g_{44}\dot{x}_4} = 0, \quad (\rho = 1, 2, 3). \quad . \quad (18)$$

Now it is easily seen that these equations are invariant for any transformation of the parameter $\lambda$. Choosing $\lambda = x_4$, we obtain precisely the Fermat equations (11) and our result is established.

Trinity College, Dublin,
June 15th, 1925.

---

CI. *A Study of a Certain Type of Air Discharge-Tube at the Critical Resistance for Flashing.* *By* James Taylor, *M.Sc., A.Inst.P., Earl Grey Memorial Fellow, & Rockefeller International Fellow, Paris, and* Leonard A. Sayce, *M.Sc., A.I.C., Armstrong College, Newcastle-upon-Tyne* *.

*Introduction.*

THE work here presented is an extension of that given in a previous paper †. One of the discharge-tubes described in the above paper was again employed. It comprised two electrodes of molybdenum wire, 3·4 cm. long, parallel to one another and separated by a distance of 0·8 cm. The condensers used were free from appreciable

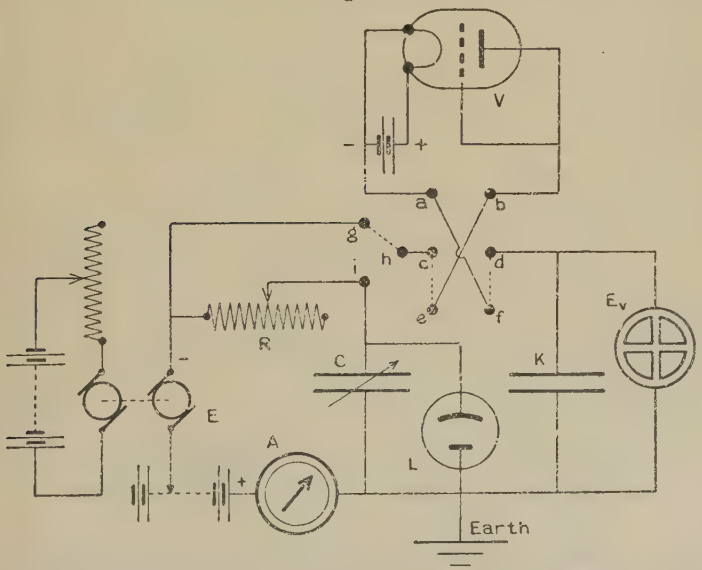
* Communicated by Prof. G. W. Todd, M.A. D.Sc.
† Taylor & Clarkson, Phil. Mag. xlix. p. 336 (Feb. 1925).

leakage, and an M-L Magneto Syndicate "Anode Converter" was utilised to generate a voltage free from grave variations and commutator ripple. The voltage from the converter could be supplemented when required by the addition of a battery of cells.

By utilising a method described elsewhere * it was possible to measure both the apparent lower and upper critical voltages when the tube was flashing at the critical resistance just before the conditions of steady discharge obtained ; this is an obvious advance on the previous work, where no such measurements could be made.

The electrical factors in the experimental arrangement are indicated in fig. 1, where E, the voltage supply, was arranged

Fig. 1.




as already described. R was a non-inductive variable resistance (0 to 3 megohms), C the capacity across the discharge-tube (L) terminals, and A a unipivot microammeter. The electrostatic voltmeter $E_v$ (Kelvin multicellular type) was shunted by a stabilizing capacity, K, of 0·3 $\mu$.F., and was associated with a double-pole double-throw switch *abcdef* and a single-pole single-throw switch *ghi*. When the poles *gh* and *cd* were connected, the voltmeter $E_v$ indicated the charging voltage E of the discharge-tube circuit. The apparent lower critical voltage $V_B$ of the tube was shown when the poles *ih*

* Taylor & Sayce, Journ. Scient. Instrs. ii. no. 9 (June 1925).

were connected and the double-pole double-throw switch was in the position *cedf*, and the upper critical voltage $V_C$ when it was in the position *acbd*. When the discharge became steady, there was no observable difference in the reading of the voltmeter when the double-pole double-throw switch was changed from one position to the other. This reading gave the lower critical voltage for the steady discharge *.

Every component of the apparatus was mounted on paraffin blocks to ensure the necessary insulation.

The air contained in the discharge tube and exhausting apparatus was dried by phosphorus pentoxide.

The experimental difficulties encountered in the actual discharge-tube work were exactly similar to those described previously, and the same methods were used to surmount them. It was found useful to employ the $\gamma$-rays from radium bromide as an external ionizing agent. In this manner erraticity of the value of the upper critical potential, due to lag of the discharge behind the voltage tending to produce it, was overcome, and results were both definite and repeatable †.

After preliminary work, it was concluded that the tube was unsuitable for the investigation of the critical resistance functions for large capacities. The conductance was small, and the flash from a large capacity was of long duration (sometimes as great as several seconds). Under these circumstances the capacity itself acted as a voltage source, and flashing frequently occurred upon the unoccupied portions of the cathode after the main discharge had become steady, due possibly to small variations of the voltage constants at different portions of the electrodes.

### *Resumé of the Previous Work on the Upper and Lower Critical Voltages for Single Flashes.*

It is perhaps advisable at the outset, in view of considerable extensions and modifications, to redefine precisely the terms and their exact connotation as employed in the present paper. It is considered necessary to alter one or two of the terms used in previous papers. The symbols in which ambiguity may arise are given below, together with their meanings.

$V_b$ and $v_c$ are used for the lower and upper critical voltages for steady discharge across the tube electrodes, whilst $V_B$ and $V_C$ are employed for the apparent values of the lower and

* Taylor & Clarkson, Phil. Mag. *loc. cit.* p. 352.

† Taylor & Sayce, *loc. cit.*

upper critical voltages, as measured on the peak-voltmeter principle, for conditions of continuous flashing. $V_b'$ is employed for the value of the extinction voltage at which the glow-discharge *just ceases* when the tube is flashing at the critical resistance immediately before the steady discharge sets in, and this corresponds theoretically with the intercept I, of the E, $R_c$ graphs.

In some recent work * the variation of the apparent lower and upper critical voltages for single flashes has been examined theoretically and practically for the neon lamp and the present type of air discharge-tube. The following general theoretical considerations were put forward. (The revised nomenclature, as defined above, is used.)

(1) The capacity C microfarads, charged to a potential of E volts, is placed across the discharge-tube electrodes, and a Townsend current flows through the tube. If a quantity of electricity $q_1$ is used up in establishing the glow-discharge, the potential V across the tube electrodes when the actual glow begins is given by

$$V = E - \frac{q_1}{C}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(2) The condenser now discharges through the tube in the form of a glow-discharge, down to the extinction voltage $V_b'$ for the discharge. This lower critical voltage is given, on certain assumptions, by the relation †

$$V_b' = F + V_a', \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where F is a constant, and $V'_a$ is the cathode fall of potential at the end of the period of flash. In cases where the full area of the cathode is employed in discharge, and the initial current is such as to give an abnormal cathode fall of potential,

$$V_a' = V_a + \phi(V, C.), \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\phi(V, C)$ represents a lag in the cathode fall of potential behind the normal value $V_a$ that would be assumed if the conditions were continuous. It is to be observed here, that recent work appears to point to the fact that the cathode fall of potential $V_a$ is different from and less than the cathode fall for the steady discharge, if small capacities are across the tube electrodes. In the paper to which reference has been made, it was assumed that $V_a$ was of constant value, independent of the magnitude of the capacity across

* Taylor & Stephenson, Phil. Mag. xlix. no. 294 (June 1925).

† *Cp.* Taylor & Clarkson, Journ. Scient. Instrs. i. no. 6, p. 174 (1924).

the tube electrodes; but this does not, in the light of recent work, appear to be the case. The above lag $\phi(V, C)$ becomes zero for normal current densities.

(3) At the end of the luminous period there is still a space-charge to be cleared up, and this results in a quantity transference $q_2$ and a further reduction of the voltage across the condenser. The apparent lower critical voltage, as measured, is

$$V_B = V_b' - \frac{q_2}{C}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $V_b'$ is given by the above relations.

In the case of large capacities, the second term of equation (4) will be small compared with the first, so that the equation may be approximated to the form,

$$V_B = V_b' = F + V_a'. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

(4) It was shown, further, that the minimum voltage across the condenser required to produce the single flash or discharge (apparent upper critical voltage) is given by the relation,

$$V_C = v_c + \frac{q_1}{C}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

When large capacities are utilized, the second term of equation (6) becomes small compared with the first term, and the equation may be approximated to the form $V_C = v_c$. It must be noted, however, that in the experiments the $\gamma$-rays from radium bromide were utilized as external ionizing agent, so that the conditions of ionization within the tube previous to a flash occurring were constant, and the lag of the discharge behind the voltage tending to produce it was suppressed.

The above relations were obtained for the physical conditions of single flash. It now remains to be seen how these will be affected when flashing is continuous, being produced in the normal way by a capacity shunted across the tube and charged from a source of potential through a high resistance R.

### *The Theory of the Variation of the Critical Constants under Conditions of Continuous Flashing.*

By James Taylor.

For large capacities and for slow flashes the theory for the variation of the critical constants will be exactly similar to that put forward for the single flash. The main difference

between the phenomena for a single flash and for continuous flashing lies in the fact that in the latter case the capacity C is continually charging up from the voltage source E, to which it is connected. This will introduce considerable modifications into the theory in the cases where small capacities are being considered.

*The Sequence of Phenomena.*

The condenser C, across the terminals of the tube, charges up from the charging voltage E through the resistance R, until a discharge through the tube occurs. Prior to the actual luminous discharge there will be a gradually increasing dark discharge whereby the current through the tube is built up to the value required for glow-discharge. Let $\theta(C, V)$ be the current-voltage function through the tube at any instant ; then to establish the glow-discharge a quantity of electricity $q_1$, given by

$$q_1 = \int_0^{t_1} \theta(C, V) \, . \, dt, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

will be expended, where $t_1$ is the time required to establish the glow-discharge. During the same interval of time a quantity of electricity,

$$\int_0^{t_1} \frac{E-V}{R} \, . \, dt,$$

flows into the condenser, *via* the circuit resistance R, from the battery. The net voltage reduction sustained by the condenser during the establishment of the glow-discharge will be given by the relation,

$$\Delta V = \frac{1}{C}\left[\int_0^{t_1} \theta(C, V) \, . \, dt - \int_0^{t_1} \frac{E-V}{R} \, . \, dt\right] . \quad . \quad (8)$$

Now the minimum voltage required to initiate discharge (*i. e.* the apparent upper critical voltage $V_C$) * will be given by $(v_c + \Delta V)$, where $v_c$ is the normal upper critical voltage required to initiate steady discharge. Introducing the value of $\Delta V$ obtained from equation (8), we have,

$$V_C = v_c + \frac{1}{C}\left[\int_0^{t_1} \theta(C, V) \, . \, dt - \int_0^{t_1} \frac{E-V}{R} \, . \, dt\right] . \quad (9)$$

The flash occurs at this instant.

* *Cp.* Taylor & Stephenson, Phil. Mag. *loc. cit.* p. 1086.

The actual time of flash will be prolonged by the quantity that flows from the circuit into the condenser C during the flash. This will modify the voltage-lag function $\phi(V, C)$. If $t'$ is the time period for a single flash, and $t''$ the time for one flash under continuous flashing conditions, then it is easily shown that $t'' > t'$, so that we should expect this effect to diminish the lag of the cathode fall behind the normal value.

When discharge down to the extinction voltage $V_b'$ has occurred, the space-charge is still to be cleared up, and this results in a quantity transference $q_2$, given by

$$q_2 = \int_0^t f(C, V) \, . \, dt,$$

where $f(C, V)$ is the current-voltage function and $t$ the time required for the clearing up of the space-charge. During the same time a quantity has run into the condenser from the external circuit, and taking this into account, it is evident that the net depreciation $\delta V$ of the voltage across the capacity due to this clear-up effect is given by

$$\delta V = \frac{1}{C}\left[\int_0^t f(C, V) \, . \, dt - \int_0^t \frac{E - V}{R} \, . \, dt\right] . \quad . \quad (10)$$

From equation (10) we see that the apparent lower critical voltage will be given by the relation,

$$\begin{aligned} V_B &= V_b' - \delta V \\ &= V_b' - \frac{1}{C}\left[\int_0^t f(C, V) \, . \, dt - \int_0^t \frac{E - V}{R} \, . \, dt\right] . \quad (11) \end{aligned}$$

It is obvious from a consideration of equation (11) that $V_B$ never can attain values as small as those obtained with very small capacities for the single flash (equation 4) because of the negative term in the expression for $\delta V$.

*The Critical Resistance Condition.*

The conditions for cessation of flashing must obtain in a region of stability of the volt-ampere characteristic of the tube: that is to say, the critical resistance condition cannot be established in the region concerned with the clearing up of the space-charge. It is thus only in the stable region of actual glow-discharge that the critical resistance condition may obtain. Under these circumstances it is evident that in the equation

$$R_c = \frac{E - V_b'}{\psi(V_b')} * \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

* Taylor & Clarkson, Phil. Mag. *loc. cit.* p. 309.

expressing the relation, the term $V_b'$, as already pointed out in the notation given above, will be the extinction voltage at which the glow-discharge just ceases when the tube is flashing at the critical resistance immediately before the steady discharge sets in. It will be shown later that this voltage may differ both from $V_b$ and $V_B$, and is subject to considerable variation with change of the pressure conditions.

Previous to the cessation of flashing, the current registered by the microammeter A (fig. 1) is an average, because the discharge is discontinuous. At the critical resistance, however, the current increases abruptly in magnitude and becomes steady. The value of this current $i_c$ at the critical resistance is of some importance, as it provides confirmation of the relation of equation (12).

The general expression for the critical resistance of equation (12) may be put into the form,

$$SR_c = E - I, \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where $S = \partial E/\partial R_c$, the slope of the graphs showing the relation between the charging voltage E and the critical resistance $R_c$, and I is the intercept of the graph on the voltage axis.

Now, when steady conditions have been attained, we have evidently,

$$i_c = \frac{E - V_b}{R_c}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (14$$

where $i_c$ is the current at the critical resistance when flashing has just ceased, E is the charging voltage, and $V_b$ is the lower critical voltage for the tube under steady discharge.

We may substitute the value of $R_c$ obtained from equation (12) into (14), and we have finally,

$$i_c = S[1-\beta], \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where $\beta = \dfrac{V_b - I}{E - I}$.

From a consideration of equation (15) it is evident that there are three distinct cases to be considered, as follows :—

(*a*) If $I > V_b$, in which case $\beta$ is negative, $i_c$ increases as E is decreased (see graphs 1, 1 *a*, 2 *a*, and 4 *a* of fig. 5).

(*b*) If $I = V_b$, in which case $\beta$ is zero, $i_c$ is constant with change of E.

(*c*) If $I < V_b$, in which case $\beta$ is positive, $i_c$ will decrease with decrease of E (see graphs of fig. 4 and graph 2 *e* of fig. 5).

These theoretical deductions are well supported by the experimental results when the values of S and I obtained from the E, $R_c$ graphs are introduced into equation (15) to obtain the functions showing the variation of $i_c$ with E.

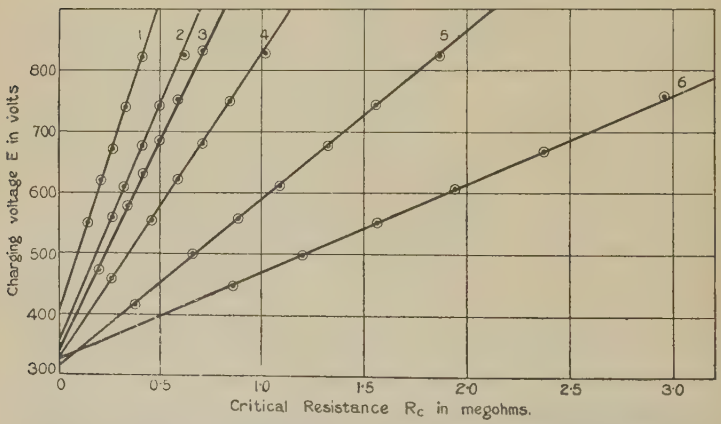
*The Experimental Results on the Measurements of the Critical Constants under Continuous Flashing Conditions.*

By James Taylor and Leonard A. Sayce.

*The Critical Resistance Relations.*

The critical resistance relations were examined for a range of capacities from 0·1 $\mu$.F. downwards, at various pressures (see graphs of figs. 2 and 3).

Fig. 2.




Graphs showing the Relationship between the Charging Voltage E and the Critical Resistance $R_c$ for a capacity of 0·1 $\mu$.F., at various pressures. [Graphs 1 to 6 of Table I.]

It would appear very occasionally as if there were two critical resistances of slightly different magnitude for the tube, but results on this point could not be obtained with any precision, owing to the relative rarity of their occurrence.

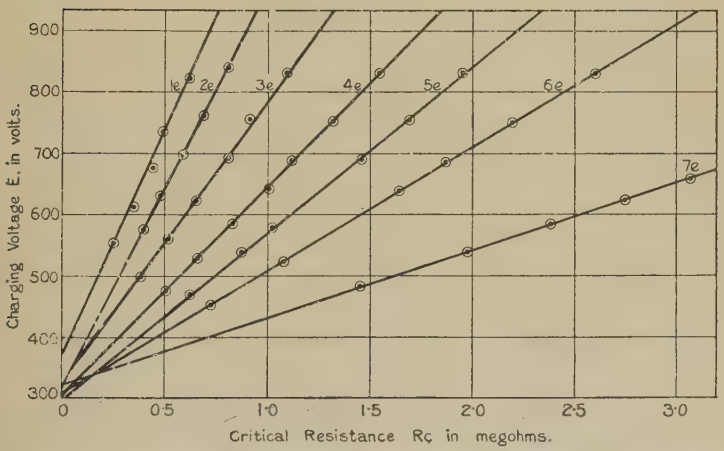
From a consideration of the data obtained (see Table I.), the following general results were found to obtain :—

($a$) The graphs showing the relation between the critical resistance $R_c$ and the charging voltage E are all linear to a high degree of approximation (the graphs of figs. 2 and 3 are typical). The linearity of the graphs was much more

precise than in the previous work (Taylor and Clarkson, *loc. cit.*), and they may all be represented by the general empirical relation of equation (13).

(*b*) The intercept I, of the E, $R_c$ graphs on the axis of voltage and theoretically of the value $V_b'$, was found to vary from values equal to $V_B$ to values well above $V_b$ *. The slopes and intercepts of the graphs are shown in Table I.

Fig. 3.




Graphs showing the Relationship between the Charging Voltage E and the Critical Resistance $R_c$ for a capacity of 0·00015 $\mu$.F., at various pressures. [Graphs 1*e* to 7*e* of Table I.]

There is a general tendency for the intercepts to be of greater value than $V_b$ at the higher pressures employed (that is, when the conductivity of the tube is greatest) and to be of the value $V_b$ or less at the medium and lower pressures employed. This classification is by no means complete.

That this variation of the voltage intercept is genuine and definite is supported by the results on the variation of the steady current at the critical resistance, with the charging voltage E. The graphs of figs. 4 and 5 show the relationship between the current at the critical resistance and the charging voltage E (a few examples only are given for illustrative purposes) [the graphs are those derived theoretically from a consideration of equation (15), and the points are from experimental data]. In every case investigated

* *Cp.* Taylor & Clarkson, Phil. Mag. *loc. cit.* pp. 345, 347.

the general trend of the results was predictable from the equation (15), and in most cases the actual agreement was very satisfactory.

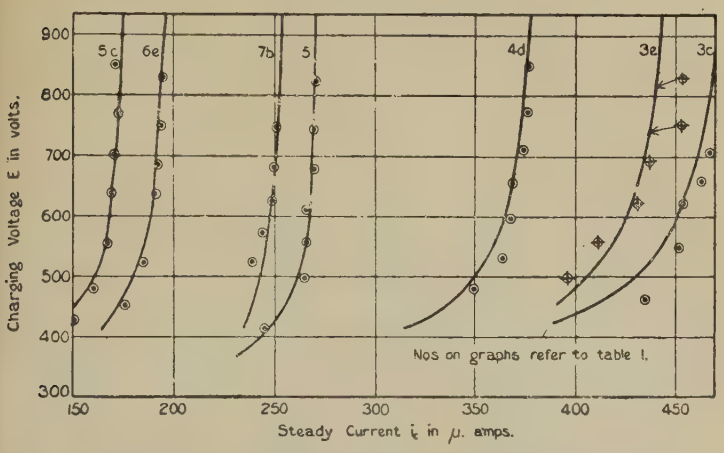
TABLE I.

Molybdenum-wire Electrode Discharge-tube.

Length of electrodes = 3·4 cm. Distance apart = 0·8 cm.

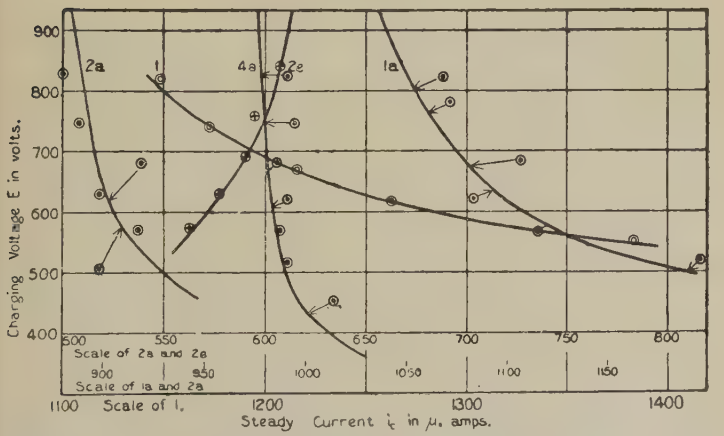
| No. of graph. | P, pressure. mm. | C, capacity. $\mu$F. | slope of graph. $\mu$ amp. | I, intercept. $\mu$ amp. | $V_b$. volts. | $V_B$ range. volts. |
|---|---|---|---|---|---|---|
| 1 ..... | 4·26 | 0·1 | 1018 | 405 | 354 | 353 |
| 2 ..... | 2·82 | 0·1 | 782 | 354 | 350·5 | 345 |
| 3 ..... | 2·10 | 0·1 | 690 | 342 | 343·5 $\pm$1 | 341 |
| 4 ..... | 1·57 | 0·1 | 500 | 327 | 327 $\pm$1 | 324 |
| 5 ..... | 1·07 | 0·1 | 275 | 314 | 324 $\pm$1·5 | 319 |
| 6 ..... | 0·64 | 0·1 | 144 | 326 | 322 $\pm$2 | 318–320 |
| 1 *a* ..... | 3·56 | 0·05 | 1005 | 378 | 355·5 | 349–351 |
| 2 *a* ..... | 3·00 | 0·05 | 872 | 363 | 354 | 346–348 |
| 3 *a* ..... | 2·32 | 0·05 | 733 | 331 | 339 $\pm$2 | 331–334 |
| 4 *a* ..... | 1·80 | 0·05 | 596 | 334 | 330 $\pm$0·5 | 327·5 |
| 5 *a* ..... | 1·57 | 0·05 | 479 | 327 | 328 $\pm$1 | 324 |
| 6 *a* ..... | 0·79 | 0·05 | 172 | 313 | 326 $\pm$3·5 | 314–319 |
| 1 *b* ..... | 4·54 | 0·005 | 1581 | 350 | 343·5 $\pm$1 | 334–340 |
| 2 *b* ..... | 3·43 | 0·005 | 1072 | 350 | 347 $\pm$1 | 338–340 |
| 3 *b* ..... | 2·58 | 0·005 | 792 | 356 | 348·5 $\pm$0·5 | 338–329·5 |
| 4 *b* ..... | 2·22 | 0·005 | 718 | 340 | 344 $\pm$1 | 331–333 |
| 5 *b* ..... | 1·82 | 0·005 | 599 | 330 | 334·5 $\pm$0·5 | 323·5–325·5 |
| 6 *b* ..... | 1·46 | 0·005 | 418 | 318 | 329·5 $\pm$1·5 | 317–318·5 |
| 7 *b* ..... | 1·05 | 0·005 | 258·5 | 317 | 328·5 $\pm$1·5 | 314–318·5 |
| 1 *c* ..... | 3·30 | 0·001 | 1127 | 322 | 345·5 $\pm$2 | 323–328 |
| 2 *c* ..... | 2·80 | 0·001 | 862 | 332 | 350 | 328–330 |
| 3 *c* ..... | 1·76 | 0·001 | 491 | 310 | 334 $\pm$2 | 311–314 |
| 4 *c* ..... | 1·27 | 0·001 | 298 | 310 | 326 $\pm$1·5 | 309 |
| 5 *c* ..... | 0·92 | 0·001 | 179·5 | 316 | 335 $\pm$1·5 | 313–318 |
| 6 *c* ..... | 0·78 | 0·001 | 141 | 329 | 336·5 $\pm$1 | 316–323 |
| 7 *c* ..... | 0·57 | 0·001 | 117·7 | 328 | 334 $\pm$2 | 322–326 |
| 1 *d* ..... | 3·94 | 0·0004 | 980 | 358 | 360 $\pm$1 | 328–332 |
| 2 *d* ..... | 2·96 | 0·0004 | 806 | 340 | 357·5 $\mp$0·5 | 325–328 |
| 3 *d* ..... | 1·96 | 0·0004 | 497 | 334 | 345 $\pm$1 | 314–317 |
| 4 *d* ..... | 1·60 | 0·0004 | 387 | 320 | 336 $\pm$1 | 310–312 |
| 5 *d* ..... | 1·30 | 0·0004 | 289·5 | 309 | 329·5 $\pm$1 | 304–306 |
| 6 *d* ..... | 0·65 | 0·0004 | 114·7 | 330 | 329·5 $\pm$0·5 | 308–315 |
| 1 *e* ..... | 4·24 | 0·00015 | 746 | 366 | 357 $\pm$1 | 306–320 |
| 2 *e* ..... | 2·84 | 0·00015 | 650 | 316 | 351 | 306–308 |
| 3 *e* ..... | 2·10 | 0·00015 | 459 | 324 | 344·5 | 301–304 |
| 4 *e* ..... | 1·57 | 0·00015 | 341 | 305 | 330·5 $\pm$1 | 296–298 |
| 5 *e* ..... | 1·32 | 0·00015 | 272 | 297 | 327 | 293–296 |
| 6 *e* ..... | 1·07 | 0·00015 | 201·5 | 306 | 326 | 291–295 |
| 7 *e* ..... | 0·67 | 0·00015 | 109·3 | 323 | 326·5 $\pm$1·5 | 305–309 |

Fig. 4.




Graphs showing the Relationship between the Steady Current $i_c$ at the Critical Resistance, and the Charging Voltage E.

Fig. 5.




Graphs showing the Relationship between the Steady Current $i_c$ at the Critical Resistance, and the Charging Voltage E.

*Measurement of the Apparent Upper and Lower Critical Voltages.*

It was found that, provided adjustments were made carefully, the values of the apparent upper and lower critical voltages could be determined at the critical resistance, just before the discharge became steady, for flashing was usually

maintained for a sufficiently long time to effect measurements. The determination of the apparent upper critical voltage $V_C$ was relatively simple: the double-pole double-throw switch *abcdef* (fig. 1), originally on the $V_B$ side (poles *ih*, *ac*, and *bd* connected), was switched over to the $V_C$ side (poles *ce* and *df* connected), and the reading in this position, of the electrostatic voltmeter $E_v$, gave the upper critical voltage value. The voltage across $E_v$ and K could be made less and adjusted to any suitable value by touching the case of the voltmeter with the hand, when leakage occurred and the $V_C$ reading could be checked by redetermination. If the double-pole double-throw switch was then put over to the $V_B$ position again, a discharge from the condenser K occurred, and this usually caused the current through the tube to become steady, and made the determination of the lower critical voltage a matter of some difficulty. It was ascertained that a combination of a very high resistance (graphite line on ebonite strip) and tapping key, placed in parallel with the valve, could be utilised for adjusting the potential across K to be just greater than $V_B$. By this means measurements were effected conveniently.

Experiment showed that the upper and lower critical voltage values did not vary much in the immediate neighbourhood of the critical resistance, so that if any difficulty was experienced in obtaining flashing at the actual critical resistance, the resistance was increased by a few thousand ohms (an amount negligible compared with the magnitudes of $R_c$ usually obtained), and the voltages then determined.

*Experimental Results on the Variations of* $V_B$ *and* I.

From a consideration of Table II., showing the variation of the apparent lower critical voltage $V_B$ with the capacity, for fixed pressures, it is seen that $V_B$ decreases with C, at first slowly, as if the relation were linear and of small slope, and then rapidly with decreasing capacity. These variations are to be expected from theoretical considerations (equation 11). In two cases (see Table II., columns 3 and 4) a slight increase of $V_B$ with decreasing capacity occurs; this increase is small, however, even when compared with the increase of $V_b$ which occurs during the same interval. In the case of very small capacities ($>0{\cdot}005$ $\mu$.F. (circa)), values of $V_B$ of less magnitude are obtained, but these are never so small as those obtained for single flashes under the same conditions *. This is in accordance with the considerations based upon equation (11).

* Taylor & Stephenson, Phil. Mag. *loc. cit.*

TABLE II.

| C. $\mu$F. | Pressure = 4·32 mm. | | | 3·26 mm. | | | 2·32 mm. | | | 1·76 mm. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $V_B$ | $V_C$. | $V_b$. | $V_B$. | $V_C$. | $V_b$. | $V_B$. | $V_C$. | $V_b$. | $V_B$. | $V_C$. | $V_b$. |
| 0·1 | 355 | 550 | 354 | 350 | 524 | 355 | 342 | 500 | 346 | 335 | 469 | 336 |
| 0·05 | 354 | 548 | 358 | 350 | 520 | 355 | 343 | 498 | 346 | 336 | 478 | 336 |
| 0·03 | 354 | 540 | 354 | 349 | 518 | 355 | 344 | 484 | 349 | 336 | 465 | 337 |
| 0·02 | — | — | — | 349 | 517 | 355 | 344 | 485 | 349 | 332 | 465 | 337 |
| 0·01 | 351 | 523 | 354 | 347 | 502 | 355 | 342 | 478 | 350 | 331 | 459 | 337 |
| 0·005 | 349 | 512 | 354 | 346 | 494 | 356 | 339 | 466 | 350 | 329 | 450 | 338 |
| 0·00476 | — | — | — | — | — | — | 338 | 465 | 350 | 329 | 449 | 338 |
| 0·00455 | — | — | — | — | — | — | — | — | — | 329 | 449 | 339 |
| 0·0033 | 347 | 500 | 354 | 344 | 483 | 356 | 335 | 460 | 351 | — | — | — |
| 0·00233 | 344 | 482 | 355 | — | — | — | 332 | 457 | 351 | 325 | 440 | 339 |
| 0·001 | 339 | 460 | 356 | 334 | 460 | 356 | 328 | 454 | 353 | 319 | 430 | 339 |
| 0·0007 | 336 | 464 | 357 | 334 | 452 | 356 | 325 | 448 | 353 | 313 | 432 | 340 |
| 0·00045 | 333 | 450 | 358 | 328 | 451 | 357 | 321 | 447 | 354 | 315 | 430 | 340 |
| 0·00024 | 330 | 459 | 360 | 318 | 470 | 356 | 315 | 449 | 354 | 308 | 432 | 340 |
| 0·00015 | 310 | 529 | 362 | 318 | 469 | 357 | 309 | 457 | 354 | 307 | 432 | 339 |
| 0·00005 | 311 | 527 | 362 | 307 | 484 | 357 | 305 | 457 | 354 | 297 | 447 | 340 |

There is not sufficient evidence to prove that $V_B$ definitely varies with the magnitude of the critical resistance, for the results obtained are almost constant within the limits of experimental error. On the whole it might appear from a consideration of the data that, where $i_c$ diminishes with decrease of E, $V_B$ either increases or is of constant value; where $i$ is constant with decrease of E, the value of $V_B$ is approximately constant; and, further, where $i_c$ increases with decrease of E, the value of $V_B$ either decreases or remains constant.

It is an interesting fact, and of considerable importance, that in the present experiments, for the range of capacities employed, the value of $V_B$ was always less than that of $V_b$. At the higher capacity values, however, the apparent lower critical voltage $V_B$ approximated to the value of the lower critical voltage $V_b$ for steady discharge. A certain proportion of the discrepancy may be accounted for by the fact that, under the experimental conditions, $V_b$ is measured when the cathode is only partially covered by the negative glow. The value of $V_b$ obtained under these conditions is somewhat different from that obtained for full cathode surface glow, and this is the condition holding for flashes. Nevertheless, there remains a real discrepancy. A consideration of equations (2) and (3) shows that the apparent lower critical voltage $V_B$ should be greater than the lower critical voltage $V_b$ for steady discharge, when large capacities are used, provided that the cathode falls of potential are identical. In certain experiments carried out on the single flash * it was found that the above conditions obtained. In the present experiments, however, it would appear that the cathode fall of potential must be less for the discharge from the capacities used, than for the steady discharge. This view is not without confirming evidence.

In the case of the smaller capacities, the discharge during flashing was definitely less intense than that obtained when the discharge was steady at the critical resistance †. The above facts would appear to indicate that the glow-discharge is characterized by a smaller lower critical voltage when small capacities are across the tube than in the case of the brighter discharge under steady conditions and when larger capacities are across the tube. This conclusion is confirmed

* Taylor & Stephenson, Phil. Mag. *loc. cit.* p. 1097.

† The steady discharge was frequently deformed at the top of the glow, as is shown in fig. 6, the end of the glow being extended into a

by direct measurements of the cathode fall of potential across the $\alpha$-particle counter for single flashes, made by Geiger *.

The results on the variation of the intercept I on the voltage axis of the graphs showing the relationship between the charging voltage E and the critical resistance are interesting. Provided the results are taken under the same pressure conditions, the intercept has greater values for the larger capacities; it appears further to be greater when the conductivity of the tube is large.

If, as was suggested in the tentative explanation of the variation of I put forward previously †, the increase in the intercept is due to an increase in $V_b'$ because of a lag in the cathode fall of potential behind the voltage across the tube, we should expect that the value of $V_B$ would increase in a manner given by the relation of equation (11), which may be put into the form,

$$V_B = 1 - \delta V.$$

On the other hand, we see from the results, that $V_B$ has values that are normal even when I has its greatest values.

---

crescent form. It was observable sometimes that the anode glow when present was more conspicuous when the discharge was continuous than when flashing was taking place.

Fig. 6.

* *Zeit. f. Phys.* xxvii. p. 7 (1924).
† Taylor & Clarkson, Phil. Mag. *loc. cit.* p. 340.

Further, from the work on the divergence of $V_B$ for the single flash in the case of the neon lamps and air discharge-tubes, it is not to be expected that the lag of the cathode fall of potential will introduce such large variations as are found at the higher pressures used in the present experiments. It must, of course, be remembered that the work on the neon discharge-tubes was carried out all at one pressure, and this makes comparison somewhat unreliable.

It was suggested in previous work that some intimate connexion may exist between the variation of the intercept I and the appearance of an anode glow. The present work has not given any real support to such a view, and that such large variations of I from the value $V_b$ should exist at the higher pressures used, still remains an anomaly. At the medium pressures the value of I coincided as well as could be expected with the value of $V_b$, and the phenomena are apparently normal in these cases. In a number of cases, however, the value of I is nearer to that of $V_B$ than $V_b$, and it would appear that in these cases the discharge during the flash is maintained to a lower potential than that characterizing the normal lower critical voltage for the steady discharge: this further suggests (as was pointed out above) that the value of the cathode fall of potential attains less values in the case of this type of discharge than in the case of the steady discharge.

*The Variation of the Apparent Upper Critical Voltage* $V_C$.

The lag in discharge behind the voltage tending to produce it is well known, and the values of the apparent upper critical voltage $V_C$ have consequently little significance unless the conditions governing the ionization in the gas within the discharge-tube, during the dark period, are maintained constant. To ensure this constancy a small quantity of radium bromide in a sealed glass tube was kept in the immediate vicinity of the discharge-tube so that the $\gamma$-rays from the radium maintained definite ionization within the filling gas. It was found that the value of $V_C$ for flashing, when the radium was used, was frequently as much as 80 or more volts less than that when the ionizing agent was removed.

From a consideration of the results showing the variation of $V_C$ with C, for different pressures (see Table II.), it is seen that $V_C$ decreases at first slowly and then more rapidly as C is further reduced, until a minimum value of $V_C$ is attained, after which it begins to increase again for further reduction of capacity. That there should be a rise in the

value of $V_C$ for very small capacities ($<0{\cdot}0004$ circa) is to be expected from the relation of equation (9), since the term in brackets is always positive and $1/C$ increases with decrease of C.

The preliminary continuous fall of $V_C$ with decrease of C is of considerable importance, for it would be expected that, provided $v$ is of constant magnitude (see equation 9), no such variation would occur. It was found that the value of the apparent upper critical voltage varies according to the quantity of the radium and its distance from the tube. This indicates that there must have been a lag effect remaining and tending to increase the value of $v_e$. That a lag effect in some form or other is responsible for the fall of $V_C$ with the magnitude of the capacity appears to be indicated by the fact that for the larger capacities where the dark period is longest, the value of $V_C$ is greatest. The results confirm the statement made in a previous paper on the critical resistance, that at the lower capacities, flashing could be maintained at values of the charging potential E considerably less than the normal upper critical voltage for the steady discharge.

*The Variation of the Lower Critical Voltage* $V_b$.

It was found from a consideration of the data that for a constant pressure and given conditions the value of $V_b$, the lower critical voltage for the steady discharge, was fairly constant. On the whole there was a tendency for an increase of a volt or two when the critical resistance was made small. It is further seen from a consideration of the results of the graphs of nos. 1 to 6, and 1 *e* to 7 *e* (figs. 2 & 3 and Table I.), which were taken at the same pressures both for the large and the small capacities, that the lower critical voltage for the very small capacities is rather more than that for the larger capacities. A similar increase is shown in the results given in Table II., where the variation of $V_b$ with capacity for fixed pressures is shown.

The explanation of the variation of $V_b$ is to be found in the fact that different areas of the electrode are employed under different conditions, the critical resistance for very small capacities being much higher than for large capacities; there is a different amount of electrode used in discharge and a slightly different critical resistance obtains, due possibly to the variation of heating effects and the distortion of the electric field between the electrodes. These variations partially account for the inaccuracies in the theoretical graphs compared with the practical ones showing the relationship between $i_c$ and E (graphs of figs. 4 and 5).

*Variation of the Mean Current when the Tube is Flashing at the Critical Resistance, with the Charging Voltage* E.

The reading of the microammeter when the tube is flashing at the critical resistance just before steady conditions obtain, is a mean between the upper and lower limits $\frac{E-V_B}{R_c}$ and $\frac{E-V_C}{R_c}$. Or, introducing the value of $R_c$ obtained from equation (12), we have,

$$\frac{E-V_B}{E-V_b'}\cdot\psi(V_b') > i_e < \frac{E-V_C}{E-V_b'}\cdot\psi(V_b'), \quad . \quad (15)$$

where $i_e$ is the reading of the microammeter for the average current. From equation (15) it can be seen that

$$\mathrm{Lt}_{E=\infty} i_e = \psi(V_b') = \partial E/\partial R_c = S. \quad . \quad . \quad (16)$$

The graph showing the relationship between the average current $i_e$ at the critical resistance when there is flashing, and the charging voltage E, will consequently approach the line $i_e = \psi(V_b')$ asymptotically.

Alternatively, the average current $i_e$ may be represented as the quotient of the total quantity transference and the total time period. This expression may be evaluated if a linear volt-ampere characteristic is assumed *, but it is extremely cumbersome in form and does not lend itself to analysis.

Let $t_1$ be the time required for the condenser C across the tube to charge up from $V_B$ to $V_C$ in the dark period, and $t_2$ be the time duration of the luminous flash. It is evident that a quantity of electricity $C(V_C - V_B)$ flows into the capacity during the dark period, and a further quantity $\int_0^{t_2} \frac{E-V}{R_c}\,.\,dt$ during the period of flash, where V is the voltage across the tube at any instant $t$. The average current is consequently given by the relation,

$$i_e = \frac{C(V_C-V_B) + \int_0^{t_2} \frac{E-V}{R_c}\,.\,dt}{t_1+t_2}. \quad . \quad . \quad (17)$$

* *Cp.* Appleton, Eneleus, & Barnett, Proc. Phil. Soc. Camb. xxii. pt. 3, p. 445 (1924).

Since $\frac{E-V}{R_c}$ varies between the limits $\frac{E-V_C}{R_c}$ and $\frac{E-V_B}{R_c}$, the above integral may be represented by $D \cdot \frac{E-V_B}{R_c} \cdot t_2$, where D is some constant less than unity. The average current $i_e$ is then given by

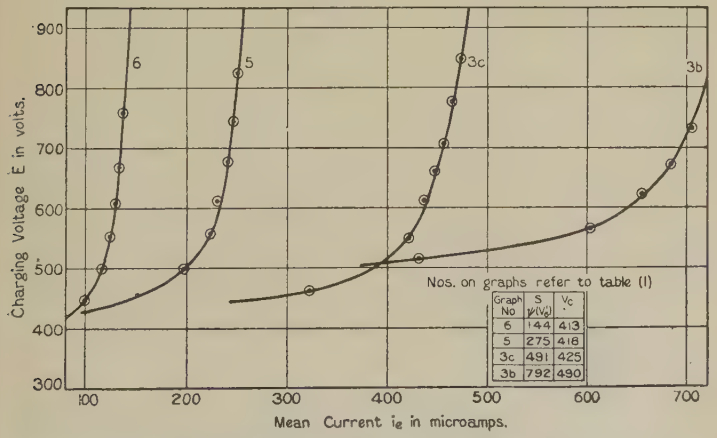
$$i_e = \frac{C(V_C - V_B) + D \cdot \frac{E-V_B}{R_c} \cdot t_2}{t_1 + t_2}. \quad . \quad . \quad (18)$$

Now it can be shown that $t_1$ increases as $R_c$ and E become less, and, further, that

$$\mathrm{Lt}_{E \to V_C} t_1 = \infty .$$

Although $t_2 \to \infty$ as $R \to R_c$, the flashes obtained for the smaller capacities in the immediate neighbourhood of the critical resistance just before steady conditions set in are not excessively slow, and it can reasonably be assumed that the value of $t_2$ is not large. It is found experimentally, in confirmation of the above, that the time period becomes

Fig. 7.




Graphs showing the Relationship between the Mean Current $i_e$ when the tube is flashing at $R_c$, and the Charging Voltage E.

greater as E is decreased (R being maintained at the critical resistance value) and the dark period comes more into prominence. It is to be expected, therefore, that $i_e$ will decrease as $R_c$ and E decrease, and that the graphs showing the relationship between $i_e$ and E will approach the line $E = V_C$, asymptotically. The graphs of fig. 7 are given to illustrate

the agreement between the practically obtained and the theoretical asymptotes, and the result is fairly satisfactory.

The authors desire to express their thanks to Prof. G. W. Todd, of Armstrong College, for his advice and assistance in the work.

*Summary.*

The paper deals with a continuation of work on the flashing of air-electric discharge-tubes in which the electrodes are near together and there is no positive column.

A method, described elsewhere (Taylor and Sayce, Journ. Scien. Instrs. ii. no. 9, June 1924), is utilised for the measurement of both the apparent lower and upper critical voltages (extinction and sparking potentials respectively) $V_B$ and $V_C$, when the tube is flashing at the critical resistance just before the conditions of steady discharge obtain.

A *resumé* of the previous work on the variation of the critical voltages for the "single flash" is given.

The variations of the critical constants for the tube under conditions of continuous flashing are discussed in a general manner, and the following general theoretical relations are put forward :—

$$V_C = v_c + \frac{1}{C}\left[\int_0^{t_1} \theta(C, V) \, . \, dt - \int_0^{t_1} \frac{E-V}{R} \, . \, dt\right], \quad (1)$$

where $v_c$ is the normal upper critical voltage for the steady discharge, C is the value in microfarads of the capacity across the tube terminals, $t_1$ is the time required to establish the glow-discharge, and $\theta(C, V)$ is the current-voltage function through the tube at any instant during this time, E the charging voltage and R the circuit resistance, and V is the voltage across the tube terminals at any instant $t$ during the interval to 0 to $t_1$.

$$V_B = V_b' - \frac{1}{C}\left[\int_0^{t} f(C, V) \, . \, dt - \int_0^{t} \frac{E-V}{R} \, . \, dt\right], \quad (2)$$

where $V_b'$ is the value of the extinction voltage at which the glow-discharge just ceases when the tube is flashing at the critical resistance, $t$ the time required for the clearing up of the space-charge etc. after the glow-discharge has ceased, $f(C, V)$ the current-voltage function during this time.

The critical resistance for flashing is further considered,

the relation being of exactly similar form to that previously derived (Taylor and Clarkson, Phil. Mag. Feb. 1925),

$$R_c = \frac{E - V_b'}{\psi(V_b')}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $R_c$ is the critical resistance below which no flashes can be obtained for the charging voltage E, and $\psi(V_b')$ is the current-voltage function for the discharge-tube at the extinction voltage $V_b'$.

The current at the critical resistance when the conditions have become steady and there are no flashes is given by the relation

$$i_c = \partial E/\partial R_c \,.\, (1-\beta), \quad . \quad . \quad . \quad . \quad (4)$$

where $\beta = \dfrac{V_b - V_b'}{E - V_b'}$.

It is shown that the graphs giving the relation between the mean current $i_e$ when the tube is flashing at the critical resistance, and the charging voltage E, will approach the lines $i_e = \partial E/\partial R_c$ and $E = V_C$ asymptotically.

The experimental section deals with the examination of these relations over a range of pressures, and the general agreement between the theoretical and practical results is found to be good. An anomaly arises in the value of the intercept I ($V_b'$) on the axis of voltage of the E, $R_c$ graphs (equation (1)), and this is discussed for different values of the capacity and pressure of the air in the discharge-tube. The variation of the apparent upper and lower critical voltages for different capacities across the tube and different pressures is discussed.

---

## CII. *Fine Structures of Spectrum Lines.*

*By* Arthur Edward Ruark *and* Roy L. Chenault *.

### *Abstract.*

Many spectral lines of non-hydrogenic atoms have fine structures which arise from transitions between the components of complex spectral levels. In none of the cases so far studied can fine structures be due to isotopy. Elements which are known to have only a single species of nucleus frequently have complex spectral lines.

In general, some of the satellites which can be predicted from

* Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

the energy diagram do not appear. In the case of thallium a fine quantum number $f$ may be introduced, with a selection principle to govern its changes, but for other elements, no selection principle has been discovered.

Fine structures have proved to be an aid in classifying spectral lines.

At present it is believed that slight quantized variations in the configuration of loosely bound underlying electron shells suffice to explain the existence of all the fine structures we have studied.

## I. *General Facts about Fine Structures; their Distribution and Origin.*

This paper deals with all available data on fine structures in the spectra of non-hydrogenic atoms. It grew out of a study of narrow doublets which appear in the arc spectrum of bismuth *.

We must distinguish between three classes of spectral phenomena which go under the name of fine structures. (1) In hydrogenic atoms there is the structure due to the relativity precession of the orbit. (2) In light atoms we encounter very narrow intervals between spectral levels which have the same total and azimuthal quantum numbers, but different inner numbers. This gives rise to narrow doublets, etc., which sometimes can be resolved only with high power spectroscopes. Such configurations have received the misleading name of fine structures. (3) There are cases in which a spectral level has several components, all characterized by the same total, azimuthal, and inner numbers This paper discusses the structure of spectral lines arising from such levels.

In what follows we shall refer to a level of this character as a *complex level*, while the term *multiple level* will designate an *ensemble* of spectral terms having the same azimuthal and total numbers, but different inner numbers.

There have been several attempts to trace regularities in the spacing of the satellites of spectral lines. Janicki † noted the similarity of certain fine structure patterns and gave an empirical formula which, in some cases, yields with precision the positions of the satellites. This formula

* Ruark, Mohler, Foote, and Chenault; "Spectra and Critical Potentials of Fifth Group Elements": Sci. Papers of the Bureau of Standards, xix. p. 463 (1924).

Ruark, Mohler, and Chenault: "Fine Structures in Non-Hydrogenic Atoms," 'Nature', cxiv, p. 575 (1924).

† *Ann. der Physik*, (4) xxix. p. 833 (1909).

is of such a kind that it cannot have any theoretical significance.

Nagaoka and his co-workers * have pointed out recurring frequency-differences in the line-structures of Hg, Cd, and Bi, many of which are real. None of these authors attempted to find the components of complex spectral levels and to trace the quantum laws which govern them.

Not many elements have been studied with high power spectroscopes, and for most of these only a few strong lines have been photographed. At least one complex spectrum line has been observed for each of the following elements :—

Cu, Cd, Hg, $Al^+$, In, Tl, Pb, Bi, Mn, Cl, Br, I, and Co.

Let us take up in order various theories as to the origin of fine structures.

1. *Isotopy.*—Nagaoka, Sugiura, and Mishima † have suggested that the satellites of spectral lines are due to isotopes. While it is possible that the existence of isotopes may account for some spectral fine structures, it can be proved that this is not the cause of the satellities in the majority of cases studied so far. Fine structures are found both in elements which consist of a mixture of isotopes, and in those which do not. Further, both isotopic and simple elements are known which have failed to show complex spectral levels in spite of thorough search. In many cases the question is settled by the variation in the relative intensity of satellites when the conditions of discharge are altered, or by their unequal behaviour in external magnetic fields. Again, we should expect that isotopy would affect all the spectral levels of a given element in approximately the same way, but all elements which have been shown to possess complex levels also have simple levels.

There is another method of settling the question of isotopic origin, which may be best understood from an example. Suppose an element consists of a mixture of two isotopes. Each energy level in the spectrum of the mixture will appear to be a narrow doublet, and the spectrum itself will be composed of narrow doublets. However, many cases are known in which two double levels give rise to

* Nagaoka and Takamine, Proc. Phys. Soc. London, xxv. p. 1 (1912). Nagaoka, Proc. Phys. Soc. London, xxix. p. 91 (1916); and Tokyo Math. Phys. Soc. Proc. viii. p. 571 (1916). Nagaoka and Sugiura, Astrophys. Journ. liii. p. 338 (1921).

† Japanese Journal of Physics, ii. Nos. 6–10 (1923).

three or four fine-structure components. In such a case, the duplicity of the levels cannot be due to isotopy *.

2. *Varying orientations of the nucleus.*—One of us has discussed the alterations in the fine structures of hydrogen and of ionized helium which are to be expected if the hydrogen nucleus or the alpha particle has an intrinsic magnetic moment of the order of $\frac{e}{2m} \cdot \frac{h}{2\pi}$ †. The calculations given are partly incorrect, but a reconsideration of the problem shows that the conclusion is unaffected; that is, the alterations of fine structure caused by the magnetic moment do not exist.

Pauli ‡ has suggested, with reservations, that fine structures in non-hydrogenic atoms may be due to deviations of the nuclear field from the inverse square law of force, caused by the complicated structure of the nucleus; he supposes, for example, that the impulse moment of the nucleus does not vanish, and that it is so placed that the impulse moment of the whole atom assumes quantized values. This assumption leads to frequency differences of the proper order of magnitude. If it is further assumed that the relative motion of the electronic and nuclear structures is a uniform precession around the vector representing the total impulse moment of the atom, a simple theory of the possible quantized states leads us to expect that complex levels will resemble tiny multiplet levels, which is sometimes true, but not always. Pauli states that these assumptions as to the origin of satellites require that in an external magnetic field they should undergo a transformation. In weak fields they should have a new and perhaps complicated Zeeman pattern, which should change, in stronger fields, into the anomalous Zeeman pattern appropriate to the spectral line in question. He enumerates some data which are in qualitative agreement with these predictions; however, other patterns are known which do not behave in the manner described.

* Harkins was probably the first to suggest the existence of changes in atomic spectra due to variations in the weight of the nucleus. Such changes have been detected by Aronberg and by Merton. Working with a large grating, Aronberg found a difference of ·0044Å between the wave-lengths of 4058 Å obtained from ordinary lead and radio lead (Astrophys. Journ. xlvii. p. 96, 1918). Merton (Proc. Roy. Soc. A, xcvi. p. 388, 1920) measured shifts of the same order of magnitude for 4058 Å and several other lead arc lines.

† Ruark, "The Hydrogen Balmer Series and the Impossibility of Further Corrections to the Quantizing of Hydrogenic Atoms," Astrophys. Journ. lviii. p. 46 (1923).

‡ *Naturwissenschaften*, xii. p. 741 (1924).

Again, if this view be correct, we should expect that all lines of a given spectral series would exhibit the same type of fine structure. This is decidedly not the case.

Pauli was careful to state that his discussion does not amount to a proof, and that his hypothesis may be completely in error. Our conclusion is that his hypothesis does not suffice to explain the majority of the observations. It would be premature to suggest a detailed mechanism to account for the complexity of spectral levels, but we shall examine the supposition that fine structures are due to variations of the configuration of underlying electron shells

3. *Variations in the Configuration of the Electron-Orbits.*—Pauli has expressed the following view : it is reasonable to assume the configuration of the inner electron groups as fully determinate when ordinary series spectra are being emitted, so that it is unsatisfactory to look for the origin of the satellites in a number of states of these electron groups with slightly different energy values. We believe that there are grave objections to this view, from the standpoints of both theory and experiment.

First, all the elements which have been shown to possess fine structures, with the exception of $Al^+$, lie in those parts of the periodic table in which either the valence shell or the next underlying shell is well on its way to completion. Thus the existence of complex spectral levels is generally associated with the presence of a large number of loosely bound electrons in the atom *.

Beyond a doubt, small quantized variations of the configuration of the outer shells can cause alterations of the energy levels of the light-electron. For example, consider an atom having several valence electrons, which, in the normal state, are on orbits belonging to a multiple level with comparatively small separations. A very slight excitation will suffice to shift several of these electrons to other levels of the multiple term, and the change in screening will result in a change in the energy of any one of these electrons. Many cases are known in which two or more electrons are on excited orbits simultaneously. The difference between this state of affairs and that which could give rise to complex spectral levels is probably one of degree, and not of kind. If the change of screening due to the excitation of additional electrons is large, we get new multiple levels, like the $p'$ and $d'$ terms of second

* The single exception to this rule, namely, the complexity of certain levels of $Al^+$, is probably caused by relativistic variation of mass. Further details are given in Section II.

group elements ; if it is small we may get fine structures, which in certain elements bear a close resemblance to tiny multiplets. However, we must not conclude from this that *all* fine structures are due to varying orientations of electron-groups with respect to each other. It is not desirable, nor do we think it possible, to refer all complex levels to a common origin.

Again, an electron in an *underlying* shell may be shifted across a small energy difference (*e. g.*, a relativity interval) with similar results. The multiple electron transitions suggested by Grotrian * to account for the non-Ritzian terms of neon are of a character similar to the processes here considered.

An important point is this : fine structures are quite capricious in their occurrence. They appear in copper; so far they have not been found in silver, a member of the same family. Mercury is rich in complex spectral levels, and some of its levels have many components, while the homologous element cadmium has relatively simple fine structures and comparatively few complex levels.

In homologous elements having fine structures, corresponding spectral levels do not show the same type of complexity. For example, 6439Å, $2P-3D$ of Cd, is sharp and single, while 5790Å, the corresponding line of Hg, is very complex. This supports our statement that the existence of complex levels depends on the dynamics of the individual element, not on a mechanical basis common to all the elements of a given group.

Table I. shows the nature of most of the spectral levels which have been critically examined. The absence of an

Table I.—The Character of Spectral Levels.

| Element. | Levels involved in the emission of simple lines. | Complex levels. | References and Remarks. |
|---|---|---|---|
| Na ..... | $1s$, $2p_{1,2}$ | ..... | Janicki, *Ann. d. Phys.* xxix. p. 833 (1909); Wali-Mohammad, Astrophys. J. xxxix. p. 185 (1914). |
| Cu ..... | ..... | $X_1, X_2, 1s?$, $2p_1?$, $2p_2?$ | Wali-Mohammad, Back. |
| Ag ..... | $3s$, $4s$, $2p$, $3d$, $4d$, $5d$ | ..... | Janicki, Wali-Mohammad. |
| Mg..... | $1S, 3S, 2P, 4D$, $5D$, $6D$, $2s$, $2p$,$3d$ | ..... | ,, ,, |

* *ZS. für Phys.* viii. p. 116 (1921).

Table I. (*continued*).

| Element. | Levels involved in the emission of simple lines. | Complex levels. | References and Remarks. |
|---|---|---|---|
| Ca ..... | ..... | ..... | Janicki examined about 50 lines. All were simple. |
| Zn ..... | $3S$, $2P$, $3D$, $4D$, $2s$, $2p$ | ... .. | Wali-Mohammad. |
| Cd ..... | $2P$, $3D$, $4D$, $3S$ | $3d_2$ ?, $2p_{1,2,3}$, $2s$ | |
| Hg ..... | ..... | ..... | This element will be discussed in another paper. |
| Al ..... | $1s$, $2p_{1,2}$ | ..... | Janicki, Wali-Mohammad. |
| $Al^+$ ... | ..... | $4F$, $4f_{1\ 2,3}$ | Paschen, *Ann. d. Phys.* lxxi. p. 537 (1923). |
| In ..... | ..... | $2p_{1,2}$, $\alpha$, $6d_2$ | $\alpha$ lies at 10647·2 cm.$^{-1}$. |
| Tl ..... | | $2s$, $2p_{1,2}$, $3d_2$. | |
| Sn ..... | ..... | ..... | 4524 and 5631 Å are simple. Narayan, 'Nature,' cxii. p. 651 (1923). |
| Pb ..... | $2p_1$, $3d_{1,2,3}$ | $2p_2$ ?, $2s$ ? | At least one of the levels $2p_2$ and $2s$ is complex. |
| Bi ..... | ..... | $\eta$, $\zeta$, $3D_1$, $3d_1{}^B$, $\alpha$ | |
| Cr ..... | ..... | ..... | 54 lines were investigated by Janicki and Wali-Mohammad. All are simple. |
| Mn ..... | d-levels at 42300–42885 cm.$^{-1}$ ($mP+C$). | $1S$, $2P_{1,2,3}$, $D^x_{1,2,3,4}$, d-level at 10524 cm.$^{-1}$. | |
| Br ..... | ..... | ..... | Kimura studied 14 complex lines. |
| I ..... | ..... | ..... | Wood and Kimura studied many complex lines. |
| Co ... .. | ..... | ..... | Wali-Mohammad found 25 lines to be simple. 4629·5 has one satellite. |
| A ..... | ..... | ..... | No complex lines. Gehrcke and v. Baeyer, *Ann. d. Phys.* xx. p. 269 (1906). |

entry in the column of complex levels does not mean that they are absent ; no element has been exhaustively examined up to the present.

## II. *Digest of Data on Fine Structures.*

Where it is necessary to distinguish the components of a complex spectral level, we shall use lower case Roman letters, beginning with the component of smallest wave-number ; thus the $2p_1$ level of thallium has two components, called

$$2p_1\text{a and } 2p_1\text{b}.$$

Except where otherwise stated, differences of wave-length are recorded in milli-ångströms and differences of wave-number in terms of the unit $10^{-3}$ cm.$^{-1}$

It is impracticable to give full references. Authorities are frequently in conflict, and no apologies are made for the arbitrary choices of data which are often necessary. In general, preference is given to measurements with crossed spectroscopes, and to grating measurements. Many satellites are left unclassified because they can originate in several ways. No attempt is made to force the interpretation beyond the limits warranted by the data. In this paper we are content to point out the fields most suitable for future research.

In this section we shall analyse nearly all the available data on fine structures, with the exception of those for mercury. This element requires detailed discussion, particularly because of the complicated Zeeman effects of its satellites, and will be dealt with in another paper.

### $Al^+$.

Paschen * observed that the levels $4F$, $4f_1$, $4f_2$, and $4f_3$ of $Al^+$ are double. He designated these pairs of orbits as $4F^a{}_1$, $4F^b{}_1$, etc. Their separations, and the number of doublets measured, are given in Table II.

Table II.

| Term. | Wave-number. | $d\nu$ in cm.$^{-1}$ | No. of doublets measured. |
|---|---|---|---|
| $4F$ ..... | 28392 | 0·489 | 4 |
| $4f_1$ ..... | 28439 | 0·100 | 4 |
| $4f_2$ ..... | 28442 | 0·490 | 5 |
| $4f_3$..... | 28444 | 0·254 | 3 |
| $4R/16$... | 27430 | | |

*These fine structures are probably due to relativity.* We can calculate the relativity correction for these orbits by

* *Ann. d. Phys.* lxxi. p. 537 (1923).

Sommerfeld's formula. Let $R$, $\alpha$, be the Rydberg number and the constant $\frac{2\pi e^2}{hc}$ respectively, while $k$ and $n'$ are the azimuthal and radial quantum numbers. $Z$, the effective nuclear charge, is computed from the term magnitudes. $Z^4=1{\cdot}075$ for the terms $4f$, and $1{\cdot}071$ for the term $4F$.

With this notation the relativity correction for a hydrogenic orbit characterized by the quantum numbers $k$ and $n'$ is,

$$\Delta\nu=\frac{R\alpha^2Z^4}{(k+n')^4}\left(\frac{1}{4}+\frac{n'}{k}\right).$$

With $Z^4=1{\cdot}075$, $k+n'=4$, we get

$$\Delta\nu=0{\cdot}3920\left(\frac{1}{4}+\frac{n'}{k}\right)$$

| | |
|---|---|
| $n'=0$ gives | $\Delta\nu=0{\cdot}0980$ cm$^{-1}$ |
| 1 | 0·2284 |
| 2 | 0·4897 |

With $n'=2$ the predicted separation for $4F$ is $0{\cdot}4879$ cm.$^{-1}$

These numbers agree well with Paschen's measured separations; the deviations of the first, third, and fourth are well within the limits of observational error, though this is not true for the second number, 0·228. If these coincidences be accepted as genuine, the interpretation would be as follows:—

All the orbits under discussion are 4-quantum orbits; the levels with smaller wave-number, designated by the superscript "a," have no relativity precession. The orbits designated by "b" are closely similiar to the "a" orbits, but are capable of carrying out a relativity precession with speed determined by the ratio of two integers $n'$ and $k$. These integers are *not* to be interpreted as the azimuthal and radial quantum numbers; they are simply integers which enter the relativity correction for the energies of $Al^+$ orbits in the same way as the azimuthal and radial numbers of hydrogenic atoms.

We have no prejudices in favour of this explanation, but thought it best to call attention to it. In case these separations are due to relativity, it is reasonable to suppose that they would not be altered by an external magnetic field.

*Cadmium.*

The following lines are simple:

6439 Å, $2P-3D$

4662 Å, $2P-4D$

5154 Å, $2P-3S$.

Hamy * and Janicki † mention a weak satellite of 6325 Å, $2P-3d_2$, and it seems reasonable to believe that this is due to complexity of the level $3d_2$.

The triplet $2p-2s$ has structures all of which contain the frequency difference 0·398 cm.$^{-1}$ pointed out by Nagaoka ‡. We give in Table III. measurements and intensities due to Takamine § as well as intensities listed by Wali-Mohammad.

Table III.

| λ Classification. | $d\lambda$. | Intensity: Takamine. | Intensity: Wali-Mohammad. | $d\nu$ |
|---|---|---|---|---|
| 5086, $2p_1-2s$ ..... | +77 | 2 | 2 | −297 |
| | 0 | 10 | 10 | 0 |
| | −25 | 2 | 1 | + 97 |
| 4800, $2p_2-2s$ ..... | +59 | 3 | 6 | −256 |
| | 0 | 10 | 10 | 0 |
| | −33 | 1 | 3 | +143 |
| | −80 | 2 | 6 | +347 |
| 4678, $2p_3-2s$ ..... | +31 | 4 | 3 | −141 |
| | 0 | 10 | 10 | 0 |
| | −57 | 2 | 6 | +260 |

*Indium.*

Uhler and Tanch ‖ studied the arc spectrum of indium in the second and third orders of a 21-foot grating spectrograph, and measured the fine structures of the following lines :—

2957 Å, $2p_1-\alpha$
2775 Å, $2p_2-\alpha$
2306 Å, $2p_2-6d_2$
2836 Å, ?

The energy level $\alpha$ does not belong to any of the four main doublet sequences. A common frequency difference, 0·509 cm.$^{-1}$, in the patterns of 2957 and 2836 Å makes it probable that 2836 involves the orbit $2p_1$. The levels $2p_1$, $2p_2$, and possibly $6d_2$ are complex. The data do not permit a complete analysis of the structures, so they are not listed

* *C.R.* cxxx. p. 489 (1900).
† *Ann. d. Physik*, xix. p. 36 (1906).
‡ Proc. Phys. Soc. London, xxix., p. 91 (1916).
§ Proc. Tokyo Math. Phys. Soc. viii. p. 51 (1915).
‖ Astrophys. J. lv. p. 291 (1922).

here. In the case of all four lines, separations are found which are in integral ratios.

*Thallium.*

Back* photographed the lines 5352, 3776, and 2767 Å, with a large grating, obtaining the results shown in Table IV.

TABLE IV.

| λ. | Intensity. | $d\nu$. | Classification. |
|---|---|---|---|
| | | | $2p_1-2s$: |
| 5352·184 | 8 | | bb |
| | | 595 | |
| 2·014 | 3 | | aa |
| | | 140 | |
| 1·974 | 10 | | ba |
| | | | $2p_2-2s$: |
| 3776·888 | 3 | | ab |
| | | 402 | |
| 6·830 | 10, double ? | | bb |
| | | 710 | |
| 6·729 | 8 | | ba |
| | | | $2p_2-3d_2$: |
| 2767·913 | 5 | | ac |
| | | 404 | |
| 7·882 | 4 | | bc and ab |
| | | 392 | |
| 7·852 | 3 | | bb |
| | | 248 | |
| 7·833 | 3 | | ba |

An energy diagram illustrating these data is given in fig. 1.

The separation 403 is evidently characteristic of the $2p_2$ level; let us suppose that 710 is the separation of two components of the $2s$ level. This leads to the result shown in fig. 1. The separations involved are very closely in integral ratios

$$140 : 403 : 710 = 1 : 2{\cdot}86 : 5.$$

The separation 392 is identical with 403 within the accuracy of the measurements, while

$$248 : 392 = 1{\cdot}90 : 3 = 2 : 3.$$

There is still other evidence for the correctness of this arrangement, as compared with another which could be suggested. Integers may be assigned to the levels as shown in fig. 1. We shall call these integers *fine quantum numbers*, and shall designate them by the letter $f$. The observed transitions correspond in every case to a change of $f$ by $+1$ or 0.

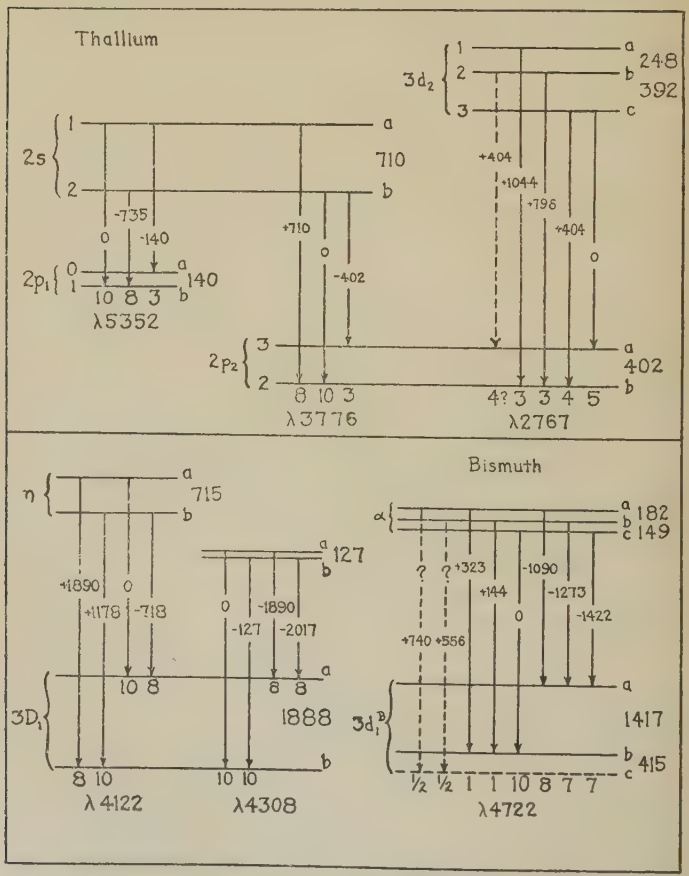
* *Annalen d. Phys.* lxx. pp. 333–372 (1923).

The absolute values of $f$ were determined so that the intervals of $3d_2$ obey a rule like that of Landé for the separation of multiple levels. That is, the interval between levels having fine quantum numbers $f_1$ and $f_2$ is assumed to be proportional to

$$f_1 + f_2 + 1.$$

Fig. 1.

Fine Structure of the Complex Levels of Thallium and Bismuth.




The letters *a*, *b*, *c* are used to designate components of complex levels. Separations (in $10^{-3}$ cm.$^{-1}$) are given on the right. Fine quantum numbers are placed to the left of each level. Intensities on a scale of 10 are indicated by numbers placed below the arrows indicating transitions, while numbers on the arrows show distances of satellites from the main line in $10^{-3}$ cm.$^{-1}$.

### *Copper.*

This element has fine structures which are very similar to those of thallium. Copper has a pair of inverted metastable levels,

$$m\,d_2 = 49062{\cdot}6 \text{ (called } x \text{ by Fowler).}$$

$$m\,d_1 = 51105{\cdot}0.$$

The lines 5782 and 5700 Å, ending on the level $md_2$, exhibit well the laws of the fine quantum number, as we may see from the data of Wali-Mohammad:—

| 5782 Å, $md_2 - 2p_2$ | | | 5700 Å, $md_2 - 2p_1$ | | |
|---|---|---|---|---|---|
| $d\lambda$ | $d\nu$ | $d^2\nu$ | $d\lambda$ | $d\nu$ | $d^2\nu$ |
| 0 | 0 | | 0 | 0 | |
| | | 172 | | | 166 |
| −57·5 | +172 | | −54 | +166 | |
| | | 114 | | | 105 |
| −95·5 | +286 | | −88 | +271 | |

Just as in the case of $3d_2$ of thallium, the separations of $md_2$ of copper are in the ratio 2 : 3. Guided by analogy with thallium, we expect the larger separation, 169, to occur in the level $2p_2$. Such is the case; the components 3274·867 and 3274·848 have the separation 175. In thallium the basic separation of which all others are multiples is approximately 128, and $\Delta 2s$ is about $6 \times 128$. In copper, therefore, we expect that $\Delta 1s$ will be about 6 times the basic separation 56; *i. e.*, it will be 336. This agrees well with either of the differences 333 or 317, as measured in the pattern of $1s - 2p_1$ by Back:

| 3248 Å, $1s - 2p_1$ | | | 3274 Å, $1s - 2p_2$ | | |
|---|---|---|---|---|---|
| λ. | Int. | $d\nu$. | λ. | Int. | $d\nu$. |
| 3248·499 | 5 | | 3274·914 | 6 | |
| | | 333 | | | 227 |
| ·463 | 10 | | ·890 | 6 | |
| | | 317 | | | 218 |
| ·430 | 6 | | ·867 | 6 | |
| | | | | | 175 |
| | | | ·848 | 4 | |
| | | 650 | | | 620 |

Further speculation is useless. The fine structures of the unclassified arc lines 4704 and 4275 Å have differences which are represented also in the patterns of known arc lines, viz., 327 and 263.

*Lead.*

Janicki *, Lunelund †, and Wali-Mohammad ‡ studied a number of lead lines. Of these the only ones which have been classified § are

4058 Å, $2p_2-2s$; complex,

4019, 4062, and 4168 Å, $2p_1-3d_{1,2,3}$; simple.

The pattern of 4058 Å exhibits separations which are in the ratio 4 : 5, as follows :

| Int. | $d\lambda$. | $d\nu$. |
|---|---|---|
| 3 | +33 | −200 |
| 10 | 0 | 0 |
| 2 | −41 | +249 |

Aronberg ‖ working with a large grating found only one satellite, at −·049 Å.

The following enhanced lines are of special interest:—

| 5372·70 Å. | | | 4245·42 Å | | |
|---|---|---|---|---|---|
| Int. | $d\lambda$. | $d\nu$. | Int. | $d\lambda$. | $d\nu$. |
| 4 | $+166_3$ | −578 | 4 | $+77_5$ | −432 |
| 4 | $+079_4$ | −275 | 4 | $+37_0$ | −206 |
| 10 | 0 | 0 | 10 | 0 | 0 |
| 3 | $-111_9$ | +388 | 3 | $-51_7$ | +288 |

Janicki noticed that the pattern of 4245 can be derived by multiplying the $d\lambda$'s of 5372 by 0·465. The ratio of corresponding $d\nu$'s is equal to 4/3 with surprising exactness.

*Bismuth.*

A few bismuth lines have been very thoroughly investigated, both with crossed interference spectroscopes, and with a 10-inch Michelson grating (by Aronberg ¶). Nagaoka and Sugiura ** give a *résumé* of the literature. Most of the frequency differences pointed out by Nagaoka and Sugiura are spurious.

* *Ann. d. Phys.* xxix. p. 833 (1909).
† *Ann. d. Phys.* xxxiv. p. 505 (1911).
‡ Astrophys. J. xxxix. p. 185 (1914).
§ Thorsen, *Naturwissenschaften*, xi. p. 78 (1923).
‖ Astrophys. J. xlvii. p. 96 (1918).
¶ Astrophys. J. xlvii. p. 102 (1918).
** Astrophys. J. liii. p. 339 (1921).

The Bi spectrum has many close doublets, due to the fact that a spectral level called $3D_1$ has two components, $3D\,^{A}{}_{1}$ and $3D^{B}{}_{1}$ separated by an interval of 1·89 cm.$^{-1}$. Nagaoka and Sugiura's data on lines involving this difference are given in Table V.

TABLE V.

| λ, Classification. | $d\lambda$. | Int. | $d\nu$. | Classification. | Remarks. |
|---|---|---|---|---|---|
| 4122, $3d_1-\eta$ | −321 | 8 | +1,890 | ab | For classifications, see Sci. Papers of Bur. of Standards, xix. p. 463 (1924). |
| | −200 | 10 | +1,178 | aa | |
| | 0 | 10 | 0 | bb | |
| | +122 | 8 | −718 | ba | |
| 4308, $3D_1-\zeta$ | 0 | 10 | 0 | ba | Intensities for 4308 are estimated from drawing, Astrophys. J. liii. p. 354 (1921). |
| | +024 | 10 | −127 | bb | |
| | +129 | 2 | −695 | | |
| | +254 | 2 | −1,368 | | |
| | +351 | 8 | −1,890 | aa | |
| | +374 | 8 | −2,017 | ab | |

The analysis of these patterns is shown in fig. 1. The data do not permit us to classify the two weak components of 4308 Å, or to determine fine quantum numbers.

The data given in Table VI. for Bi 4722 Å are those of Nagaoka, Sugiura, and Mishima. The only doubtful component is that for which $d\lambda = +179$.

TABLE VI.

| λ Classification. | $d\lambda$. | Int. | $d\nu$. | Classification. |
|---|---|---|---|---|
| 4722 $3d^{B}{}_{1}-\alpha$ | −328 | 1 | +1,470 | |
| | −279 | 1 | +1,250 | |
| | −218 | 3 | + 978 | |
| | −165 | 0·5 | + 740 | ca |
| | −126 | 0·5 | + 556 | cb |
| | − 78 | 1 | + 323 | ba |
| | − 32 | 1 | + 144 | bb |
| | − 0 | 10 | 0 | bc |
| | + 57 | 8 | − 256 | |
| | +102 | 6 | − 458 | |
| | +179 ? | 1 | − 803 ? | |
| | +243 | 8 | −1,090 | aa |
| | +284 | 7 | −1,273 | ab |
| | +317 | 7 | −1,422 | ac |

The analysis of this pattern cannot be carried out further than shown in fig. 1, unless we make unwarranted assumptions. The diagram in fig. 1 could be inverted, so far as we know.

Wali-Mohammad * found the lines 5552, 4733, and 4561 Å to be simple.

* Astrophys. J. xxxix. p. 185 (1914).

TABLE VII.

| Spectral Term. | Wave-number. | $d\nu$. | $d^2\nu$. | Remarks. |
|---|---|---|---|---|
| $1S$ | 59937 | | | |
| | | −265 | | |
| | | | 80 | |
| | | −185 | | |
| | | | 86 | |
| | | − 99 | | |
| | | | 99 | |
| | | 0 | | |
| | | | 99 | |
| | | + 99 | | |
| $2P_1$ | 24167 | −503 | | |
| | | | 140 | |
| | | −363 | | |
| | | | 168 | |
| | | −195 | | |
| | | | 195 | |
| | | 0 | | |
| $2P_2$ | 24211 | −323 | | |
| | | | 152 | |
| | | −171 | | |
| | | | 171 | |
| | | 0 | | |
| $2P_3$ | 24247 | −398 | | |
| | | | 170 | |
| | | −228 | | |
| | | | 228 | |
| | | 0 | | |
| $D^X_1$ | 18148 | −280 | | |
| | | | 76 | |
| | | −204 | | |
| | | | 96 | |
| | | −108 | | |
| | | | 108 | |
| | | 0 | | |
| $D^X_2$ | 18004 | −382 | | |
| | | | 73 | |
| | | −309 | | |
| | | | 88 | |
| | | −221 | | |
| | | | 101 | |
| | | −120 | | |
| | | | 120 | |
| | | 0 | | |
| $D^X_3$ | 17883 | −234 | | |
| | | | 111 | |
| | | −123 | | |
| | | | 123 | |
| | | 0 | | |
| $D^X_4$ | 17793 | −141 | | |
| | | | 141 | |
| | | 0 | | |
| $D^X_5$ | 17738 | - · | — | Unknown. |
| | 10524 | −497 | | Listed by Catalán as a diffuse term of the sextet system. The arrangement here given depends on only one line. |
| | | | 206 | |
| | | −291 | | |
| | | | 164 | |
| | | −127 | | |
| | | | 127 | |
| | | 0 | | |

### *Manganese.*

Wali-Mohammad* and Janicki† have studied this element. The results confirm the classifications due to Catalán, and make it possible to classify several more spectral lines. (See Section III.)

We give in Table VII. the structures of the complex levels. The separations are mean values taken from the patterns of several lines and are in good agreement with all observed values. In each case $dv$ is measured from the level belonging to the strongest line.

The $d$-levels of the sextet system between 42300 and 42885 cm.$^{-1}$ are simple. The same is true of the levels which Catalán calls $(mP+C)$.

### *Bromine.*

Kimura ‡ has studied the fine structures of 14 bromine lines between 6632 and 4674 Å. The lines 6632, 6560, 6351, and 6150 Å furnish constant differences which will be of great aid in classifying this spectrum, since they have similar fine structures.

Table VIII.

Fine Structures of Bromine Lines.

| λ. | $dv$ | | | |
|---|---|---|---|---|
| 6632 | 0 | +182 | +314 | – |
| 6560 | 0 | +186 | +332 | – |
| 6351 | 0 | +171 | +354 | – |
| 6150 | 0 | +180 | +334 | +388? |

Still other interesting relations can be found in Kimura's data. He studied also the Zeeman effect of complex bromine lines. It is very probable that all the complex lines investigated are due to neutral bromine.

### *Iodine.*

The structures and Zeeman effects of complex lines of iodine were investigated by Wood and Kimura § using an echelon crossed with a grating. There are three fine structure patterns which are repeated several times. These

* Astrophys. J. xxxix. p. 185 (1914).
† *Ann. d. Phys.* xxix. p. 849 (1909).
‡ Kyoto College of Science Memoirs, iv. p. 139 (1920).
§ Astrophys. J., xlvi. pp. 181 and 197 (1917).

should afford an excellent basis for a classification of the spectra of iodine. All the complex lines are enhanced when a capacity or a spark-gap is placed in parallel with the discharge tube.

There are interesting relationships among the separations of the components in some of the patterns. The structures of the lines 4474, 4632, and 5161 Å are similar. Table IX. gives average values for the positions and separations of the components.

TABLE IX.

Separations in Iodine Lines 4474, 4632, and 5161 Å.

| $d\nu$. | $d^2\nu$. |
|---|---|
| 0 | |
| | 393 |
| 393 | |
| | 295 |
| 698 | |
| | 225 |
| 923 | |
| | 163 |
| 1,086 | |

The numbers in the column $d^2\nu$ are in the ratios

$$5 : 3{\cdot}75 : 2{\cdot}85 : 2{\cdot}07,$$

or, approximately,

$$5 : 4 : 3 : 2.$$

The corresponding data for the lines 5245, 5345, and 5370 is contained in Table X.

TABLE X.

Separations in Iodine Lines 5245, 5345, and 5370 Å.

| $d\nu$. | $d^2\nu$. |
|---|---|
| 0 | |
| | 190 |
| 190 | |
| | 163 |
| 353 | |
| | 167 |
| 520 | |
| | 187 |
| 704 | |

Here the separations are approximately equal.

The structures of 5497 and 5464 are reproduced in Table XI.

TABLE XI.

Separations in Iodine Lines 5497 and 5464 Å.

| 5497 Å. | | 5464 Å. | |
|---|---|---|---|
| $dv$. | $d^2v$. | $dv$. | $d^2v$. |
| 0 | | 0 | |
| | 444 | | 355 |
| 444 | | 355 | |
| | 326 | | 282 |
| 770 | | 637 | |
| | 258 | | 217 |
| 1,028 | | 854 | |
| | 107 | | 66 |
| 1,135 | | 920 | |

The ratios of the numbers $d^2v$ are:

For 5497 Å, 4 : 2·96 : 2·32 : 0·965.

For 5464 Å, 5 : 3·97 : 3·06 : 0·94.

These levels are discussed in detail to show that the occurrence of integral separation ratios in a given complex spectral level is not at all rare. The phenomenon is so well developed in iodine that one cannot doubt its reality.

Of course in spectra which have not yet been classified there is a possibility that complex spectral lines are really minute multiplets. However, this seems unlikely in so heavy an element as iodine.

## III. *Spectral Classifications in Manganese accomplished by the Aid of Fine Structures.*

The fine structure of the manganese line 5399·494 Å is identical with that of several lines having the common initial level $2P_1$. This shows that it must be classified as $y-2P_1$ where

$$y=42682{\cdot}62 \text{ cm.}^{-1}.$$

A search for other lines involving this orbit yielded the following results, all of which, it is hoped, are genuine.

| Line. | λ predicted. | λ observed. | Int. |
|---|---|---|---|
| $y-2P_2$ | 5412·400 | 5412·446 | 1 |
| $y-3D$ | 3108·713 | 3108·777 | 3 |
| $y-2s$ | 4506·758 | 4506·917 | 1 |
| $y-3D^y_1$ | 3233·950 | 3234·078 | 3 |
| $y-3D^y_2$ | 3227·894 | 3228·071 | 7 |

From the line 4026·226 Å whose initial orbit is $D^x_1$ at 18148 cm.$^{-1}$ we get the new orbit

$$X = 42978{\cdot}19.$$

| Line. | λ predicted. | λ observed. | Int. |
|---|---|---|---|
| $X-1s$ | 4448·717 | 4448·753 | 3 |
| $X-2s$ | 3011·328 | 3011·378 | 2 |

The line 5388·7 may involve $D^x_1$ (=18148 cm.$^{-1}$) or $D^x_2$ (=18004 cm.$^{-1}$). The question cannot be decided at present.

## IV. *Quantum Relations in Fine Structures.*

In what precedes we have seen repeatedly that the separations of complex spectral levels are frequently in integral ratios, and that in general some of the possible satellites are not observed, as though a selection principle were operative. We attempted in all cases to assign fine quantum numbers to the various components of the complex levels and to state selection principles to govern the changes of the fine quantum number. The difficulty is that in general the data do not suffice to decide between different interpretations.

It is possible that the numbers affixed to the components of complex levels are not themselves quantum numbers, but are functions of the integers $f$ which enter into the relation $J=fh$. In any case, the fundamental postulates of the quantum theory require the existence of a quantum number whose values are characteristic of the various components of a complex level, all of which have the same total, azimuthal, and inner numbers. We are certain of the existence of such numbers even in cases where we cannot find their values.

Bureau of Standards,
Washington, D.C.
May 14, 1925.

CIII. *Sound-Changes analysed by Records.*—I. *Trumpet and Cornet. By* Prof. E. H. Barton, *F.R.S., and* H. M. Browning, *M.Sc., Ph.D.**

[Plates XXIX.—XXXI.]

MANY excellent records have been obtained of the sustained notes of various musical instruments. On the other hand, any gramophone record gives in miniature the vibrations of a whole song or other musical selection. However, there seems to be an intermediate field ripe for exploration. This, in our view, is the recording and analyzation, on a fairly large scale, of the various fundamental changes of sounds as produced on different instruments, including the human voice. That is to say, those changes which, while not constituting a musical passage, are the elements out of which all such passages are built up. These naturally include :—

(1) Changes in *loudness* of a sustained note, such as sforzando, crescendo, and tremolo, or of iterated notes in single-, double-, and triple-tongueing on those instruments that admit of such treatment.

(2) Changes in *pitch*, such as the production of various intervals, and the scale, shakes and turns, and the portamento on the instruments capable of it.

(3) Changes in *quality*, intentionally or accidentally, occurring in connexion with any of the above.

In this first paper many of the above changes have been examined as produced on the trumpet and cornet. It is hoped that later papers may deal with contrasting instruments such as the voice, the wood-wind, and strings.

It is sometimes complained that the shake and other embellishments on the brass instruments are not so close as might be desired. To the present writers it seems astonishing that the makers of trumpets and cornets have succeeded in producing instruments on which shakes can be rendered so well as is the case. The depression of the valve to produce the shake is nearly half an inch, and the passage for the new note is open before that of the old note is closed. This is essential to prevent entire interruption of the current of air from the player's lips, but obviously it leaves room for undesirable possibilities. Thus the new note may begin before the old one ceases. As to whether this often or ever occurs is one of the problems in point. And, if it does,

* Communicated by the Authors.

whether this is so distressing as might be expected, or is even noticeable at all, is another problem. It is here found that the two notes may overlap for about a tenth of a second without the musical hearer suspecting it. Many of the above-mentioned possible changes have been examined for the trumpet and cornet with amateur and professional playing, and the characteristic records of the corresponding musical elements have been obtained and reproduced.

### *Theory.*

In any one position of their valves the trumpet and cornet have free periods of oscillation of the contained air-column which nearly, but not quite, form a Fourier series. They are forced into vibrating according to a Fourier series by the human breath and lips, the latter being held in suitable tension so as to act as membranous reeds vibrating at the pitch and with the quality desired. The equations of motion of the vibrations thus produced at the mouthpiece may be written as follows (at any rate as a first approximation for small motions) :—

$$\left.\begin{aligned} &\frac{d^2y_1}{dt^2}+2k\frac{dy_1}{dt}+p^2y_1=f_1\sin(nt+\phi_1)\\ &\cdots\cdots\cdots\cdots\cdots\\ &\cdots\cdots\cdots\cdots\cdots\\ &\frac{d^2y_m}{dt^2}+2k\frac{dy_m}{dt}+(mp+h_m)^2y_m=f_m\sin(mnt+\phi_m)\\ &\cdots\cdots\cdots\cdots\cdots \end{aligned}\right\}\quad\ldots\quad(1)$$

Thus the complete solution for the $n$th term could then be written

$$y_m=\frac{f_m\sin(mnt+\phi m+\alpha_m)}{\{[(mp+h_m)^2-(mn)^2]^2+(2kmn)^2\}^{1/2}}+B_me^{-kt}\sin(q_mt+\beta_m),\quad(2$$

where

$$\tan\alpha_m=\frac{-2kmn}{(mp+h_m)^2-(mn)^2}\quad\ldots\quad(3)$$

and

$$q_m^2=(mp+h_m)^2-k^2,\quad\ldots\quad(4)$$

and $B_m$ and $\beta_m$ are arbitrary constants to be chosen according to the initial conditions. It may be seen that in the above equations $k$ is the resistance to the motion of the air particles per unit mass per unit velocity, $p/2\pi$ is the frequency of the fundamental natural to the air column, $f_1$ is the maximum value of the force per unit mass of the fundamental, $n/2\pi$ its

frequency, and $\phi$ its phase-angle. The general term is indicated by $m$ as a subscript or factor, and the $h$'s show the departures from strict commensurability of the frequencies of the partial tones of the instrument. It may be noticed that $h_1$ is supposed zero, and therefore does not appear in the first equation. Further, $k$ without a subscript is used throughout.

To justify the assumption that the problem in hand is really a case of small motions, we may note that if the instrument gives with spherical radiation at a distance of one mile a just audible amplitude of $10^{-8}$ cm., the amplitude at the bell of 10 cm. diameter would be of the order $6 \times 10^{-4}$ cm. or $6\mu$. At the throat (3 mm. diameter) of the mouthpiece the amplitude would be of the order 0·2 mm., or less than the hundredth of an inch! Thus it seems legitimate to assume that the separate equations of (1) and their solutions will simply superpose to give the actual occurrences at the mouthpiece.

Each such component vibration is associated with a separate stationary wave in the air-column of the instrument. The general term of such stationary waves in a cone open at the base and closed at the vertex may be expressed by

$$Y_m,$$

where
$$Y_m = F_m(r) y_m, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)^*$$

$r$ being the slant length from the vertex of the cone. For the actual instrument with cupped mouthpiece, hyperbolic tubing, and bell the form of the function will be still more complicated, but may be equally well represented by (5), since the precise form of the function of $r$ is left unstated.

The initial vibrations of a sustained note on a trumpet or cornet previously silent consists of two sets of vibrations, the forced and the free, the latter having such amplitude and phase as to fulfil the initial conditions. Both are compound tones, the forced being a set of strictly commensurate partials, while the free are not so, being very slightly inharmonic. This discrepancy may entail a wandering of the overtones of the resultant vibration and a fluctuation of its amplitude. Fortunately this state of things lasts for a time so short as to be almost inappreciable to the ear. This is due to the heavy damping of the free vibrations, which quickly leaves the forced vibrations in sole possession of the field. An estimate

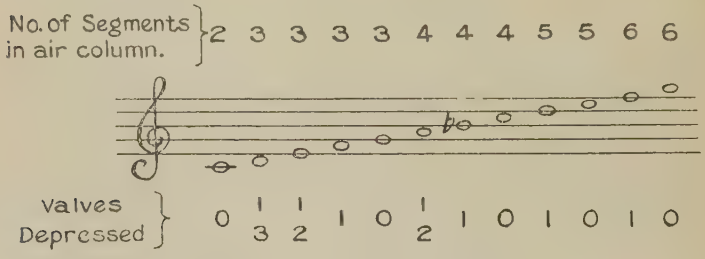
* It is known that the antinodes occur for this cone as for an open parallel pipe, but that the nodes are all displaced towards the vertex. See Rayleigh's 'Sound,' art. 281, vol. ii., or E. H. Barton's 'Sound,' fig. 51, art. 188.

made in a previous paper (see p. 140, Phil. Mag. July 1913) would give $e^{-30t}$ as the damping factor for the amplitude. Some records of the present paper make it appear still greater.

When the forcing is stopped, the free vibrations assert themselves—*i. e.*, take over the amplitude and phase then existing, and introduce their own frequency and damping. The wandering overtones may reappear, but the resultant amplitude will in the main quickly die away.

In a passage of detached notes, each one being separately "tongued" or articulated, the mechanism and phenomena approach that outlined above; but we have next to consider the changes of pitch and afterwards the modifications occurring in slurred passages. Changes of pitch always involve changes in lip-tension and air-pressure and may involve also the depression or release of one or more valves, or both actions combined. The depression of the valve puts in use a small extra crook of tubing, which lengthens the air-column in vibration and so lowers the pitch *if* the lips force this new length to subdivide into the previous number of segments. However, if the lips are used to force it to subdivide into a greater number of segments, a higher pitch may be obtained from this longer tube. This is illustrated in the following scheme in fig. 1.

Fig. 1.




Scheme of Open and Valve Notes.

As examples of changing the note without changing the valve, we have the ascending passages C G C′ E′ G′ and B♭ D′ F′. As examples of lowering the pitch by depressing the first valve and not changing the number of segments, we have G F, C′ B♭, and E′ D′. As examples of raising the pitch by depressing the first valve and increasing the number of segments, we have C′ D′ and E′ F′.

It should be noted that the tension of the lips has to be adjusted for every different pitch, and that for a given pitch

the tension is the same irrespective of the number of segments in use. Thus G on the second line may be obtained by three vibrating segments of the tube without valves, or by four vibrating segments of the longer tube in use if the first and third valves are depressed together. If the player were blindfolded he could sound the note equally well, and be unconscious which way it was being fingered if held by another person.

Now when a passage is *slurred*, two or more notes being played by a continuous emission of breath, the sound and the forcing never cease. This is possible because the valves are arranged to open the new passage before closing the old, and so obviate a total stoppage. The question then naturally arises, at what stage of the valve's motion does the pitch change. So far as the instrument is concerned, there is obviously some latitude which may lie at the player's disposal, and will vary from time to time. An ideal case would appear to be at or shortly after a valve is midway in its action. Further, since both lengths of tubing (those with and without the extra lengths due to the valve) are available for a short time, we may naturally inquire whether the notes actually overlap. Some of the records show that they occasionally do so.

## *Description of Apparatus.*

During the investigations the apparatus has been modified several times, although the essential part has remained unaltered. This is a type of phonoscope similar to that described by Mr. C. J. Lapp*. Fig. 2 (Pl. XXIX.) is a photograph of the phonoscope used. A diaphragm of thin duplicating-paper is stretched over a circular hole 7 cm. diameter in a brass plate, and is held in place by a brass ring. To the centre of the diaphragm is attached a thread of plaited silk about 0·1 mm. diameter; the other end of the thread is attached to a fine conical spring and a small wad of cotton-wool is put in this to damp out the vibrations of the spring. Across the diaphragm, 0·5 cm. above and parallel to it, is another silk thread held at one end and stretched by a spring at the other. This is passed 0·2 cm. from the perpendicular thread. A mirror 1 cm. in width and 0·6 cm. long is mounted so that its centre lies on the horizontal thread, and one edge touches the perpendicular thread, the mirror thus making an angle of 45° with the diaphragm. When a sound-wave is

* Optical Soc. of America, Jr. Rev. Sci. Inst. vii. pp. 661–664 (Aug. 1923).

caught by the diaphragm, the mirror vibrates round the horizontal thread, causing a beam of light to trace out a sound-wave form on a photographic plate or film moving in a direction perpendicular to that of the vibrating spot of light.

The chief fault of this phonoscope is that it is highly selective; thus it is impossible to use it for comparing the intensities of certain notes, or for finding the quantitative relation between a fundamental and its overtones. However, in certain cases overtones are present, and are sufficiently pronounced to show creeping during the establishment of the note and steadiness when the note is established.

In the first experiments, of which figs. 1–10 (Pl. XXX.) are photographic records, a horizontal beam of light from a parallel arc-light was directed on the mirror of the phonoscope, and then focussed vertically down by lenses on the slit of a camera as used by Mr. W. H. George*; this latter was placed on a box on the floor. At first quarter-plates and then plates 6 inches long were used, but the records were considered too short.

Next, the light was directed horizontally through a slit in a light-tight box on to a drum which was rotated, by a small clockwork motor, about a vertical axis. Films were used and longer records made, but the speed of rotation was so slow (one-sixth of a revolution, or 3 inches of film per second) that the separate vibrations were not visible. The clockwork motor was not strong enough to speed up the motion, although this was attempted (see fig. 16, Pl. XXX.). The final arrangement, which has proved very satisfactory, is shown in fig. 3 (Pl. XXIX.). Light from a pointolite lamp is directed on to the phonoscope mirror and focussed by crossed cylindrical lenses on the edge of a wooden disk about 2 inches thick placed on the table of a gramophone motor. The latter is enclosed in a light-tight box, and the light enters through a cubic chamber at one side; this is closed by a door. The speed of the motor can be maintained very nearly constant, and can be regulated within the usual limits.

Cinematograph films were used, and attached to the drum by drawing-pins. The "pointolite" was used for all the films and for the large plates. In the first experiments the cotton-wool was omitted from the spring, and this caused vibrations of frequency about 40 per second, which are seen in figs. 6, 11–14 (Pl. XXX.). In the long films the cotton-wool was used throughout.

* 'Journal of Scientific Instruments,' Oct. 1924.

The method of taking the records was for one person to produce the sounds either on a tuning-fork or brass instrument, and for a second person to expose the plate or the film at the required time. In the case of the tuning-forks the exposure was made as soon as possible after the fork was excited. For the cornet or trumpet, either the film was exposed and immediately the note was sounded (*e.g.* fig. 17, Pl. XXX.), or the notes were well started, and then the exposure was made when the quality was considered satisfactory.

Some of the sounds recorded were due to a professional cornet player, Sergeant H. Scattergood, using a Boosey cornet; these are figs. 17, 20 (Pl. XXX.) and figs. 23, 24 and 28 (Pl. XXXI.). The others are by one of the writers on a Boosey cornet or a Mahillon trumpet.

*Results.*

Figs. 5, 6, and 7 (Pl. XXX.) and fig. 22 (Pl. XXXI.) are traces of vibrations by tuning-forks. Fig. 22 shows the regularity of the speed of the drum in the gramophone motor and the slow damping of the tuning-fork; moreover, it shows no vibrations which might be due to free periods of the diaphragm. Figs. 5 and 6 are due to tuning-forks C (256 per sec.) and D (288 per sec.) separately, and fig. 7 is the result of the two superimposed, in which the beats are very pronounced. These beats being about 32 per sec. would be too quick to hear separately. (In figs. 6 and 7 a slow fluctuation is seen; this is due to the spring being undamped by cotton-wool, and so being set in motion by slight movements of the floor or walls.) These records are an indication of the value of the diaphragm as a sound-recording instrument.

The remainder of the figures are for notes either by the cornet or the trumpet.

Fig. 15 shows a long sustained note C (254 per sec.) on the B trumpet, with a crescendo in the middle and a diminuendo towards the end.

Figs. 11, 12, 14, and 17 show scales and chords with single-tongueing. In all cases the notes are quite separate from one another, but in the first three, which were notes on the trumpet, the outline only of the amplitude is seen, not the vibrations which constitute the notes. The vibrations which appear are due to lack of cotton-wool. However, in fig. 17, obtained with the gramophone motor, the separate vibrations are seen, and these increase in frequency according to the scale indicated above them in tonic sol fa notation.

This was a record of notes (403, 427, 479, 535, 604, 640 per sec.) blown by a professional cornet player.

Fig. 13 is a slurred scale, but may be compared with fig. 12 to show the positions of the various notes. In this no definite break is seen between any of the separate notes ; otherwise it is very nearly identical with the record fig. 12. They are both the ascending scale in C on the B trumpet (254 to 508 per sec.). There are two other examples of slurred notes (figs. 18 and 19). These were both taken on the B♭ trumpet. Fig. 18 shows a drop of an octave from C′ to C (480 to 240 per sec.). The original note is seen in the first twentieth of the diagram, and the change to the lower note takes considerable time, as the lower note is not definitely established until half the film has passed. This film is interesting because of the partials ; it is clear that while the note is steady the partials are commensurate, but during the change from one note to another the overtones are seen to wander. Fig. 19 shows a slurred jump from C′ to F (480 to 320 per sec.). In this case the change was quicker, and the partials not being so marked, their change is not so definite. The higher note occupies about a tenth of the film and the change about another quarter ; the lower note persists until near the end, when it is seen to die away.

Fig. 20 shows double-tongueing (*tŭ-kŭ*)* on the cornet. This figure is rather difficult to interpret ; possibly each large beat is due to one pair of notes produced by double-tongueing. Fig. 16 is a good example of double-tongueing, but has unfortunately overlapped. It may, however, be interpreted as follows :—At the arrow lettered *a* the record of a long note begins ; at *b* begins the record of six short notes produced by double-tongueing. Of these six, two reached to the end of the film, the other four occurring at the beginning of the film up to *a* ; then at *b* begins the second record of a final long note, which ended at the end of the film. This record was obtained on the slow drum, but by accident it was accelerated at the start, and so showed the separate vibrations.

Fig. 21 shows triple-tongueing. The first group of vibrations is the end of a long note and the three following sets are

* Double- and triple-tongueing are used to give clear articulation in very rapid passages. Single-tongueing is effected by drawing the tongue smartly back from the almost closed lips, so pronouncing a syllable approaching *tŭ* or *too*. But this procedure gives only one note for each double-motion of the tongue. In double-tongueing the syllables *tŭ-kŭ* are aimed at, the *kŭ* utilizing the return or forward motion of the tongue which in single-tongueing is silent. In triple-tongueing the syllables used are *tŭ-tŭ-kŭ*.

due to the triple-tongueing, *tŭ-tŭ-kŭ*. The last note was not intended to be longer than the others, but was accidentally made so.

Fig. 23 shows the record of a sforzando attack on the B♭ cornet by the professional player, the note being 480 per second. It would appear that the beats in the establishment of the full amplitude characterize this declamatory effect.

Figs. 24–27 show the traces of *turns*, an embellishment in which the main note alternates with those above and below it. Of these records the first is by the professional player on the cornet, and the others by the amateur on the trumpet. The frequencies of the main notes in the four cases are 480, 538, 538, and 403 per sec. The two of the same frequency were differently accented. Three of these four records show sets of beats for one or more notes. It would appear that from imperfect playing the note intended to be replaced by another continued to sound along with that other, and so produced the beats in question. This possibility was never detected by hearing; it was the records alone that revealed it. Thus we see that the records analyse further than the ear can do, and so reveal what may be called defects from the scientific point, though they elude detection by a musical ear.

Records of shakes are given in figs. 2–4, 8–10, and 28–35. Figs. 2, 3, and 4 are records of the shake on the low B♭ on the B♭ cornet (213 and 240 per sec.). Fig. 1 shows the upper note of this pair alone (it is C on the B♭ cornet). Fig. 8 gives the record of the shake on the low B♭ of the B♭ cornet (213 and 240 per sec., as in the short plates, figs. 2, 3, and 4). Fig. 9 gives the record of the shake on F on the A cornet (302 and 339 per sec.). Fig. 10 is the record of a shake on the higher B♭ on the A cornet (403 and 452 per sec.). All these records show that the sound is continuous but much reduced in intensity, as seen by the narrow necks of amplitude whose squares are proportional to the intensities of the notes. All these records of shakes show a number of overtones, and these overtones wander considerably during the establishment of the notes. The first note in fig. 8 has overtones fairly steady. In parts of 9 and 10 this wandering is very marked; in other parts where the note is established great steadiness is maintained. In fig. 1, showing a single note, the octave overtone is very clearly seen.

Fig. 28 shows a shake by the professional cornet player (Sergt. H. Scattergood) on the B♭ cornet, the notes being F♯ and G (339 and 359 per sec.). In this record the narrow necks appear to occur between the lower and upper notes,

the pair taking only about one-eighth of a second. In the middle of the time the notes were so loud that the record scarcely shows at all. The record of fig. 29 shows what was intended to be a shake on the C trumpet, the notes being F♯ and G (380 and 403 per sec.). The G is an open note, F♯ being produced by depressing the second valve. The photographic plate was exposed when the effect was quite satisfactory to the ears. In spite of this, the record shows that though the F♯ occurs, the G persists through it, and gives a pair of throbs instead of a steady note. Four repeats of the pattern were shown on the whole film. Figs. 30 and 31 show records of the shakes on the same notes as in fig. 29; but here the lower note seems to be reached and the upper nearly or quite extinguished. The lower note is still, as before, shorter than the upper. The two together occupy about one-fifth of a second. Even at this slower rate of the amateur's fingering (ten notes per second) the motion of the finger and the valves can differ very slightly, if at all, from simple harmonic. Hence, the instant when the note jumps from one pitch to another must be largely a matter of favouring of either, due to the pinch of the lips and the air-pressure in use. Thus the duration of the upper and lower notes are not certain to be equal.

Figs. 32 and 33 give records of shakes on the low B on the C trumpet (254 and 269 per sec.). Fig. 32 again shows inequality of duration of the upper and lower notes, while fig. 33 gives only slight indications of the junction of the two notes, which are about equal in duration and almost free from throbs, but show wandering overtones.

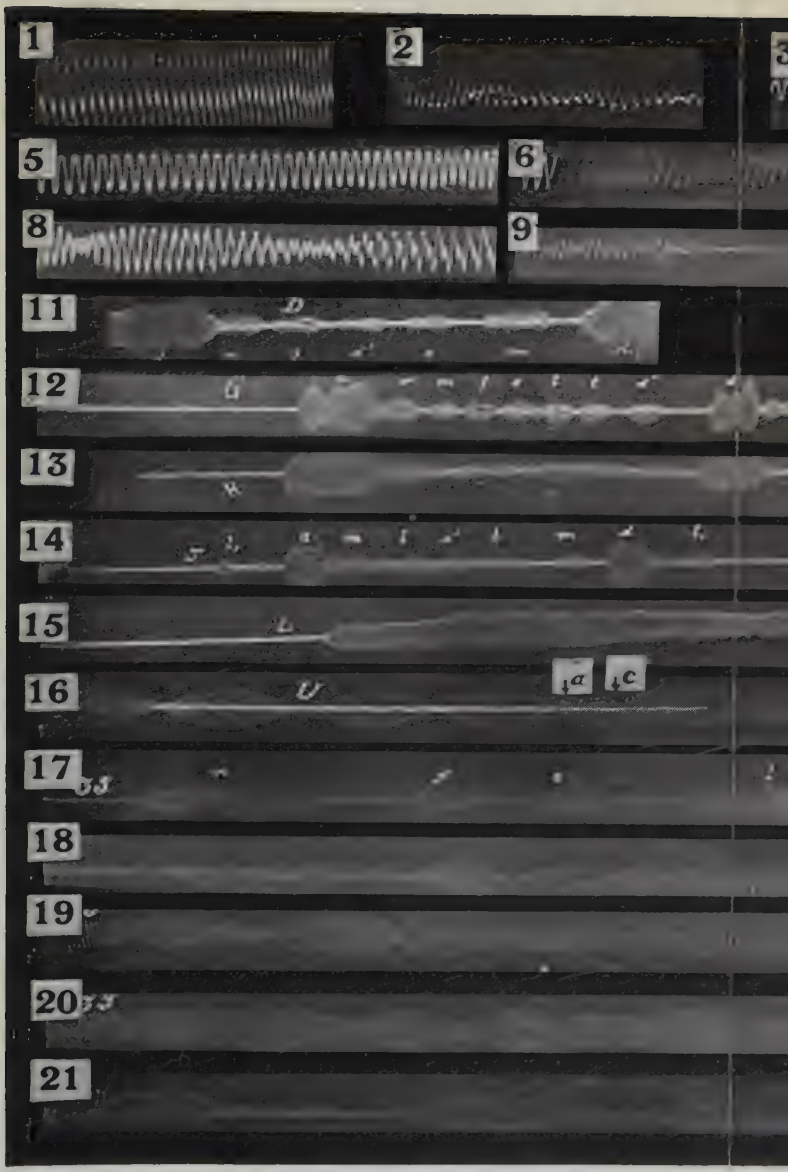
The record in fig. 34 is of a shake consisting of the notes G and A♭ on the C trumpet (403 and 427 per sec.). Like that in fig. 29, it shows a long note and a short one in two throbs, the latter being the lower note. Fig. 35 is the record of a shake consisting of G and A (389 and 403 per sec.) on the B♭ cornet. The notes used to obtain figs. 34 and 35 were chosen because for them the upper note in each case was produced by depressing the valves, the lower note being without use of valves. This is contrary to all the previous cases, and it was thought that it might prove that the valve note always showed the throbs whether lower or higher. But this did not prove to be the case. It seems to be a matter simply of which note is so far favoured by the player as to persist through the other note which should replace it.

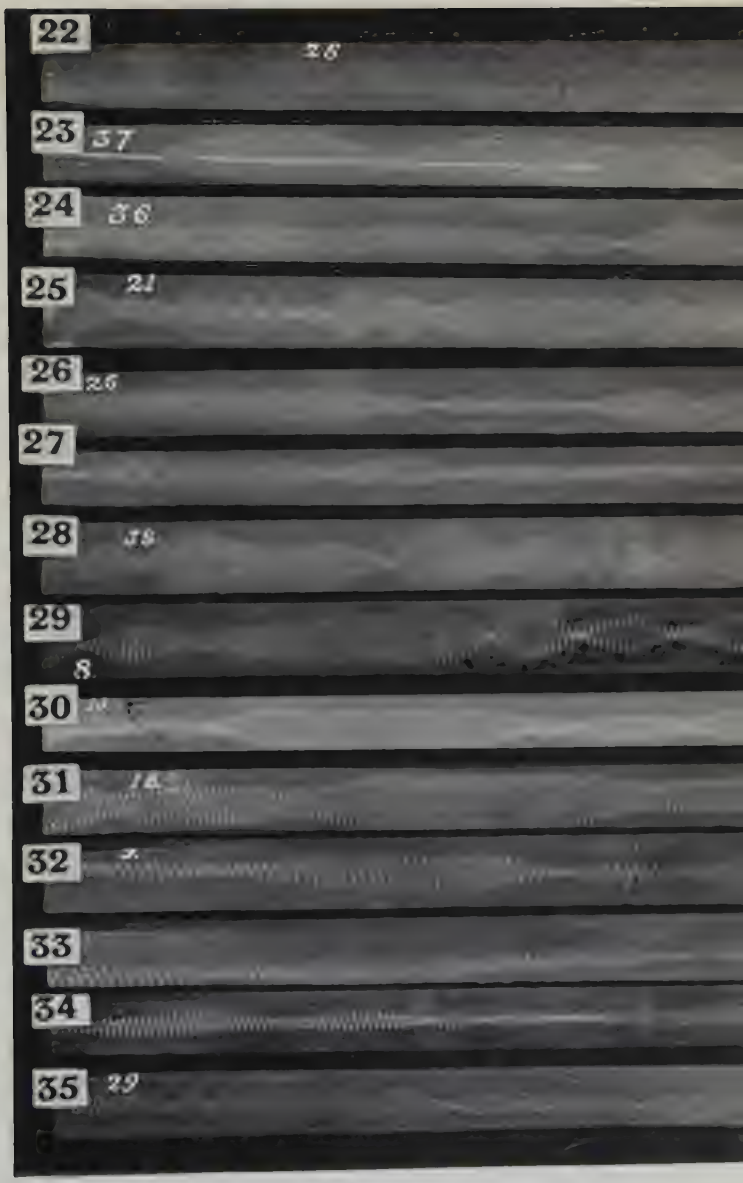
Fig. 2.

Diaphragm Mounting.

Fig. 3.

Photograph of Apparatus.


1
2
5
6
8
9
11
12
13
14
15
16
17
18
19
20
21


22
23
24
25
26
27
28
29
30
31
32
33
34
35

*Summary and Conclusion.*

The general inference to be drawn from this work is that the records analyse the amplitude more delicately than the ear. (Indeed, it is well for the acceptance of the current standard of playing that the ear is not more keenly critical.) On the other hand, the eye, when regarding the records, may easily overlook a change of pitch of a semitone; whereas this change, or less, is immediately detected by an ear listening to the corresponding sound.

Nottingham,
June 9, 1925.

---

CIV. *Diffraction by Line Screens.* *By* L. R. Wilberforce, *M.A., Lyon Jones Professor of Physics, The University of Liverpool* *.

[Plate XXXII.]

I HAVE for a long time been convinced that students of physical optics would derive much benefit from observations made with some fairly coarse form of diffraction grating in which the details of the lines and their spacing could be examined with a low-power microscope. Recently I learnt from Dr. J. R. Milne, of the Department of Natural Philosophy of the University of Edinburgh, that he shared this opinion and had met the need by the use of one of the components of a broken "line screen." These screens are employed in process photography, and consist of two similar ruled glass plates fixed so that their lines are mutually perpendicular, and I am greatly indebted to Dr. Milne for his kindness in presenting me with a piece of the plate which he had used. I found that this plate formed a grating of about 133 lines to the inch, with portions alternately opaque and transparent approximately equal in breadth. When mounted on a spectrometer and examined with sodium light, it gave a long series of spectra on both sides of the central line, all sharp and unaccompanied by "ghosts," which testified to the accuracy of the ruling. I was struck, however, by the slow falling-off in intensity of the spectra of higher orders, and still more by the fact that the spectra of even order were as strong as those of odd order, while the

* Communicated by the Author.

approximate equality of the opaque and transparent spaces should have made them at least very weak.

This led to a critical examination of the ruled plate. The lines were found to be fairly deep grooves filled in with opaque black pigment, with edges remarkably sharp, even when inspected with a microscope ; and the general planeness of the surfaces was evidently satisfactory. The ruled surface bore rubbing with dry paper or leather or linen without injury, but when a portion was washed and brushed with soap and water, the pigment was removed and the grooves revealed. They were seen to be canals with remarkably straight margins, from which the sides fell in irregularly-scored slopes towards the middle. The accompanying Plate (XXXII.) shows high-power microphotographs, A of the opaque lines and B of the washed-out grooves, which indicate the remarkable sharpness of the edges in each case and the close equality of width between the opaque and transparent portions.

A result of such accuracy and uniformity must have been produced by some kind of mechanical ruling together with subsequent etching, and it is clear that if the originally plane surfaces of the glass between the opaque portions remained unaffected by these processes, the behaviour of the grating must accord with elementary theory, and the spectra of even order should be absent or faint.

An obvious explanation of the discrepancy is that these surfaces have in some way been distorted or modified, for example by a slight rounding of their edges, and thus in the directions for the spectra of even order the light from different portions of each transparent space will have traversed slightly different thicknesses of glass, and will no longer consist of an even number of half-period elements.

It occurred to me that the validity of this explanation could be tested by putting on the ruled surface a drop of cedar-wood oil, whose index of refraction is practically equal to that of plate glass, covering the oil with a piece of similar glass whose outer surface at least was plane, and using this combination in place of the original grating, so that wherever owing to want of perfect planeness some glass was absent, an equivalent thickness of cedar-wood oil would take its place.

This experiment proved quite successful ; the spectra of even order were now only just perceptible, and the spectra of odd order fell off rapidly in intensity. The glass plate was then removed and the oil carefully wiped off the ruled surface, and it was found that the original character of the

spectra was restored. This proved that the oil had produced merely its anticipated optical effect and that the grating itself was unaltered by its use.

A contact photographic print of the ruled surface was then made on glass. In comparison with the original the opaque and transparent portions were, of course, interchanged, and the boundary between them was naturally a little less sharp. When this contact print was used as a diffraction grating, the distribution of intensity in the spectra was only slightly different from that given by the grating mounted in oil, the earlier spectra of even order being more visible while the intensities of the spectra of odd order diminished a little more rapidly. This suggested that the transparent portions of the photographic film behaved as of approximately constant optical thickness, and that the effect of a slight blurring of the edges on the intensities of the spectra though perceptible was not great.

The spectra thus obtained were photographed, and two sets of prints, C and D, are shown on the accompanying Plate (XXXII.). In each, No. 1 gives the result for the dry grating, No. 2 for the grating mounted in oil, and No. 3 for the contact print, with equal times of exposure. Unfortunately, they are unsymmetrical from right to left, but on each side the differences of character are easily seen. In D the printing was carried rather far, in order to bring out more clearly the differences between 2 and 3, and the details of the central parts are consequently obscured.

The results thus obtained are of interest in connexion with an observation by R. W. Wood, described by him on p. 225 of his well-known book on Physical Optics. He made "a contact print on a photographic plate of a grating with 400 very sharply-ruled black lines to the inch; one edge of the grating was in contact with the plate, while the other was separated from it by means of a piece of paper. The blurring [of the edges of the lines] thus increased progressively across the plate. The original grating showed the first 35 orders of spectra of a sodium flame, while the print showed but three, when the flame was viewed through the edge which was in contact with the original. As the eye was moved along the print, the 2nd- and 3rd-order spectra rapidly faded away, the first order only being yielded by the end which was separated from the original."

I hope that it is not presumptuous to point out that in a grating consisting merely of opaque and transparent spaces the spectra of order approaching the 35th would be extremely faint unless the transparent spaces were unusually narrow,

and to suggest the possibility that the original grating employed by Professor Wood may have been similar in character to mine.

Subsequently I received an introduction to Messrs. Max Levy & Co., of Philadelphia, U. S. A., the manufacturers of these line screens, who treated me with great courtesy and presented me with specimens of ruled surfaces going up to 600 lines to the inch.

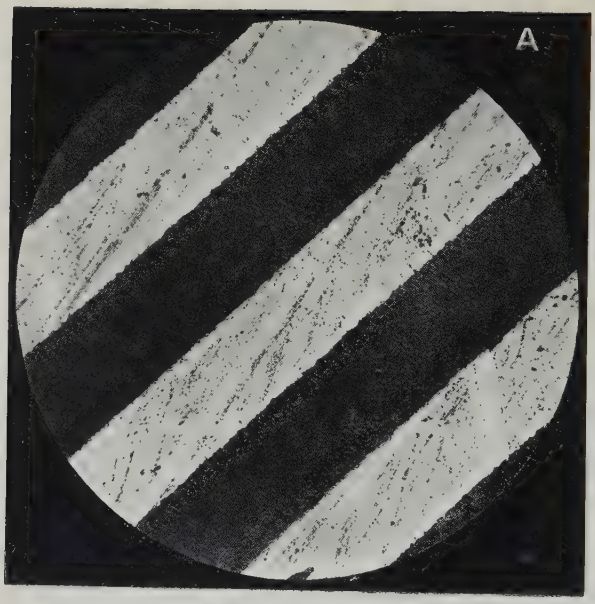
Even these more closely-ruled gratings were remarkable not only for the accuracy of their spacing, but, what must be far more difficult to secure, for the sharpness of the edges of the lines, and for the uniformity of the ratio of width of the transparent and opaque portions. I tested a number of them, alternately dry and mounted in cedar-wood oil, and the contact prints obtained from them, with results similar in character to those already described.

It may be of interest to give some details in connexion with the behaviour of one of them, of about 600 lines to the inch, in which the transparent spaces were seen to be a little narrower than the opaque, though with this closeness of ruling the boundaries were not sufficiently sharp for trustworthy measurement. When this grating was used dry, all the spectra up to about the 13th order were visible with a gradual falling-off of intensity. When, however, the grating was mounted in cèdar-wood oil, the fifth spectrum on either side was weaker than either the fourth or the sixth, the seventh spectrum was absent, and the ninth weaker than either the eighth or the tenth.

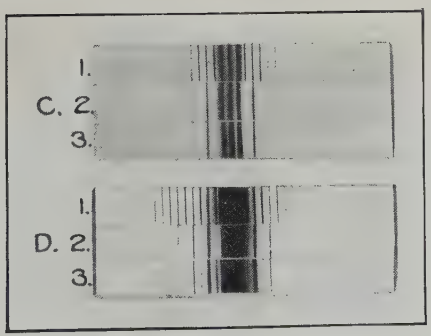
It is easy to see that such a distribution of intensity would be given if the widths of the transparent and opaque spaces were in the ratio of 3 to 4, but in that case the spectra of the second order should also be weaker than those of the third. This, however, was not observed ; possibly the blame may rest upon the irregularities of the boundaries.

It appears, therefore, that when employed by students, line screens can be made to pay a double debt as diffraction gratings. If used dry, they may show an abnormally long series of spectra, and so give angles of diffraction large enough for fairly accurate measurement, and if mounted in cedar-wood oil, they will behave like the ideal grating of elementary theory.

In conclusion, I wish to express my thanks to Mr. R. W. Roberts for the spectrum photographs and to Professor E. E. Glynn for the micro-photographs which they kindly undertook to make for me.


A

B


1.
C. 2.
3.
1.
D. 2.
3.

# CV. *The Calculation of the Equivalent Conductivity of Strong Electrolytes at Infinite Dilution.* Part I.—*Aqueous Solutions.*

*By* A. Ferguson, *M.A.*, *D.Sc.*, *and* I. Vogel, *M.Sc.**

IN the course of an examination of certain dilution formulæ it seemed to us that the equation

$$\frac{(C\alpha)^n}{C(1-\alpha)} = K, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

originally proposed by Storch †, had not, perhaps, received the consideration which it merits. In this equation the quantity $\alpha$ is at present used as a shorthand symbol for $\Lambda/\Lambda_0$, the ratio of the equivalent conductivity at the concentration C to that at zero concentration. One factor in the neglect of this equation is undoubtedly the difficulty of the determination of the constants therein by a method which shall at once be accurate and easy to use. Many of the methods employed for this and analogous equations are both difficult to handle and in some instances of very doubtful validity. It is all the more strange that cumbersome methods should continue in use, since for some years past simple methods of dealing with equations of this and of similar type have been collected and classified by Running ‡. However we may attack the problem of the determination of the constants of the Storch equation, one constant which must be accurately known is $\Lambda_0$, and in this communication we propose to discuss a method for the determination of $\Lambda_0$ which gives results of an order of consistency at least as high as those obtained by the usual methods. It is not necessary to discuss in great detail the methods previously employed, as these are reviewed in papers by Bates §, by Washburn ‖, by Lorenz ¶, and by Walden **.

It is possible to determine $\Lambda_0$ directly from the Storch

* Communicated by the Authors.

† Storch, *Zeit. Phys. Chem.* xix. p. 13 (1896).

‡ Running, 'Empirical Formulas' (Chapman & Hall, 1917). See especially p. 45.

§ Bates, Journ. Amer. Chem. Soc. xxxv. p. 519 (1912).

‖ Washburn, *ibid.* xl. pp. 122, 150 (1918).

¶ Lorenz, *Zeit. Anorg. Chem.* cviii. pp. 81, 191 (1919); cxii. p. 209 (1920); cxviii. p. 209 (1921).

** Walden, *ibid.* cxv. p. 49 (1921).

equation (1) ; for this equation may be written

$$C^{n-1}\Lambda^n = K\Lambda_0^{n-1}(\Lambda_0-\Lambda) = K_1(\Lambda_0-\Lambda)$$

or

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{1}{K_1\Lambda_0}(C\Lambda)^{n-1}. \quad . \quad . \quad . \quad . \quad (1{\cdot}1)$$

Taking $1/\Lambda$ as a new variable ($y$), and $C\Lambda$ as $x$, this equation takes on the form

$$y = a + bx^p ;$$

and, as we shall see in the sequel, an equation of this form can be treated by a definite and accurate method, permitting an unambiguous determination of the three constants $a$, $b$, and $p$ ; this, of course, determines the values of $\Lambda_0$, K, and $n$ in equation (1).

Equation (1·1) is that used by Noyes * for the calculation of $\Lambda_0$. He therefore tacitly assumes the validity of the Storch equation. But the constants of equation (1·1) are computed by an unsatisfactory and laborious process of trial and error, the value of $n$ being varied step by step and plots of $(C\Lambda)^{n-1}$ against $1/\Lambda$ made for each value of $n$. That value is finally chosen which gives most nearly a linear plot for the two variables just mentioned.

Bates† has used a similar method of trial and error, and Washburn‡ plots graphically the relation between K and C for low concentrations (where K stands for $\frac{C\Lambda^2}{\Lambda_0(\Lambda_0-\Lambda)}$), and extrapolates the curve to the axis of zero concentration, the assumption being that at infinite dilution Ostwald's dilution law holds, and K is independent of C.

As methods are known, or can very easily be devised, for testing these simple functions by grouping the variables so as to yield a *linear* plot, it seemed to the writers preferable to calculate $\Lambda_0$ by choosing some simple function which could easily be tested over ranges of concentration such that no such corrections as, *e.g.*, the viscosity correction need be considered. If such a function yields a strictly linear plot down to the lowest observed concentrations, it can be extrapolated to zero concentration with some confidence.

Of the various equations proposed, those which represent,

* Noyes, Journ. Amer. Chem. Soc. xxx. p. 335 (1908) and succeeding papers.

† Bates, Journ. Amer. Chem. Soc. xxxv. p. 519 (1912).

‡ Washburn, Journ. Amer. Chem. Soc. xl. p. 122 (1918).

at least for low concentrations, the relation between $\Lambda$ and C as

$$\Lambda = \Lambda_0 - Bf(C) \quad . \quad . \quad . \quad . \quad . \quad (1{\cdot}2)$$

seem to be the most promising. Some of the equations used by Kohlrausch are of this type, and in 1919 Lorenz* proposed the relation

$$\Lambda = \Lambda_0 - BC^n. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here, again, the difficulties of handling the equation apparently proved formidable. Lorenz, for example, assumes Kohlrausch's value of $\Lambda_0$ for sodium chloride, and then proceeds to calculate values of B and $n$ by giving $n$ in succession the values 0·33, 0·40, 0·45, and 0·50. He then finds that for $n = 0{\cdot}45$ the values of B over the range $C = 0{\cdot}0001$ to $C = 0{\cdot}02$ are fairly constant. It cannot be too strongly emphasized that this laborious and approximate procedure is quite unnecessary, and that the values of $\Lambda_0$, of B, and of $n$ can be determined very simply by an analytical method.

The equation considered is of the type

$$y = a - bx^n.$$

Suppose, then, that we are in possession of a number of values of $x$ and $y$, and require to determine the constants $a$, $b$, and $n$. The values of $x$ and $y$ are plotted out on accurate squared paper, and a smooth curve is drawn through them by means of a spline or other suitable drafting device. Choose now a number of points whose abscissæ increase in any suitable geometrical progression of common ratio $r$. Tabulate the values of $x$, the corresponding values of $y$, and the values of $\Delta y$ of the first difference of $y$. Then we have

$$\begin{aligned} y &= a - bx^n, \\ y + \Delta y &= a - b(rx)^n, \\ \Delta y &= bx^n(1 - r^n), \\ \log \Delta y &= \log b(1 - r^n) + n \log x, \quad . \quad . \quad (2{\cdot}1) \end{aligned}$$

and *a plot of* $\log \Delta y$ *against* $\log x$ *yields a straight line which determines* $b$ *and* $n$. $b$ and $n$ being known, from every pair of values of $x$ and $y$ the equation

$$y + bx^n = a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

enables one to determine a series of values of $a$ of which the resulting mean gives the most probable value.

* Lorenz, *Zeit. anorg. Chem.* cviii. p. 191 (1919).

It is obvious that an equation of the type (2) does not at any stage of the dilution formally agree with Ostwald's dilution equation. The latter formula may be written

$$\frac{C\Lambda^2}{\Lambda_0(\Lambda_0-\Lambda)} = K_2, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

if we agree that the fractional ionization is given by the ratio $\Lambda/\Lambda_0$. Re-writing equation (4) we see that it does not formally agree with equation (2), although it may very well happen that equations (2) and (4) when plotted together may coincide over a portion of their range within the limits of experimental error. Whether Ostwald's dilution formula may be considered valid in the limit is a question which is still *sub judice*. Certainly it is hardly to be expected that a formula whose logical basis is definitely statistical should be capable of extrapolation to a region of such dilution that statistical notions fail. Such an extrapolation seems to be on a level with the extension of the definition of temperature obtained from statistical considerations to the idea of the temperature of a single molecule. The utmost that can be said at the present time seems to be that there *may* be a portion of the conductivity-concentration curve which for a region of very low but finite concentrations coincides with the curve of Ostwald's dilution formula.

Although, therefore, equation (2) is not over any region of concentration in formal agreement with Ostwald's, the results of a plot between log $\Delta y$ and log $x$ are so unambiguously linear at low concentrations that we feel no hesitation in extrapolating the resulting equation down to zero concentration in order to determine $\Lambda_0$. Equation (2) is not proposed as a general dilution formula ; it is wholly employed to calculate $\Lambda_0$ for the further discussion of other dilution equations. Nevertheless, it is worth pointing out that while the equation is valid up to a concentration of 0·001 N for all the strong electrolytes investigated, for a number of classes of uni-univalent and of uni-bivalent electrolytes the formula is valid up to a concentration of 0·01 N.

As the method of computation is not, apparently, in general use, we give the full details for an aqueous solution of potassium chloride. Using Kohlrausch and Maltby's* figures, curve A in fig. 1 was plotted out and was drawn through the experimental points with the assistance of a flexible wooden spline. The ordinates ($\Lambda$) corresponding to

* Kohlrausch and Maltby, *Wiss. Abh. Phys. Techn. Reichsanstalt*, iii. p. 156 (1911) ; *Ges. Abh.* ii. p. 826 (1911).

a series of abscissæ (C) proceeding in a geometrical progression of common ratio 2 were then read off from the curve A and tabulated. The first differences ($\Delta\Lambda$) were tabulated, as were log $\Delta\Lambda$ and log C.

A plot of log $\Delta\Lambda$ against log C gave the straight line B in fig. 1. Table I. below shows the results of these operations.

Fig. 1.

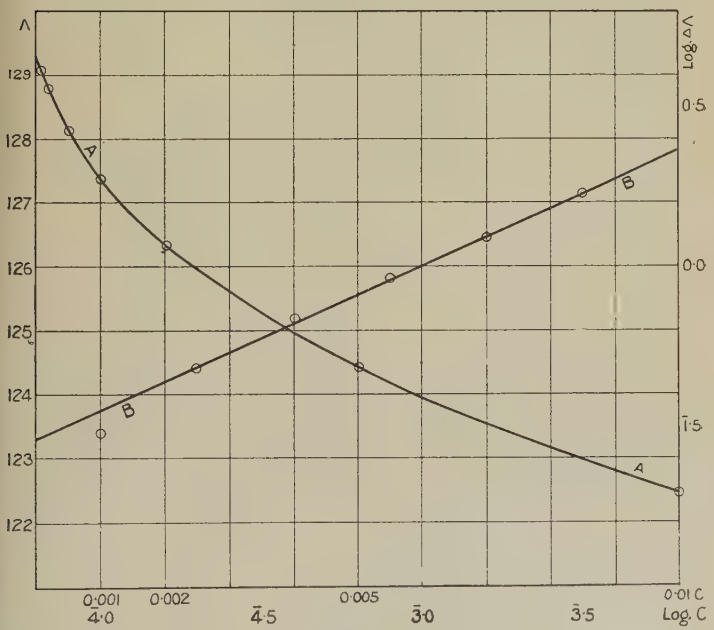



TABLE I.

| *C. | Δ. | ΔΛ. | Log ΔΛ. | Log C. |
|---|---|---|---|---|
| $1{\cdot}0\times10^{-4}$ | 129·07 | 0·30 | $\bar{1}{\cdot}47712$ | $\bar{4}{\cdot}00000$ |
| $2{\cdot}0\times10^{-4}$ | 128·77 | 0·48 | $\bar{1}{\cdot}68124$ | $\bar{4}{\cdot}30103$ |
| $4{\cdot}0\times10^{-4}$ | 128·29 | 0·69 | $\bar{1}{\cdot}83885$ | $\bar{4}{\cdot}60206$ |
| $8{\cdot}0\times10^{-4}$ | 127·60 | 0·93 | $\bar{1}{\cdot}96848$ | $\bar{4}{\cdot}90309$ |
| $1{\cdot}6\times10^{-3}$ | 126·67 | 1·23 | 0·08991 | $\bar{3}{\cdot}20412$ |
| $3{\cdot}2\times10^{-3}$ | 125·44 | 1·67 | 0·22272 | $\bar{3}{\cdot}50515$ |
| $6{\cdot}4\times10^{-3}$ | 123·77 | | | |

* Throughout this paper C will be expressed in gram equivalents per litre.

The equation (2·1) represents the straight line B. The slope of the straight line therefore gives the value of $n$, whilst the intercept on the axis of $y$ gives the value of $\log b(1-r^n)$ and as $r$ and $n$ are known this determines $b$. In this manner it was found that

$$\Lambda = \Lambda_0 - 61{\cdot}26C^{0{\cdot}452v}. \quad . \quad . \quad . \quad . \quad (6)$$

From any pair of observed values of $\Lambda$ and C we can now, using equation (6), calculate $\Lambda_0$. The results of this calculation are shown in Table II. and it will be seen that the consistency of the values of $\Lambda_0$ leaves little to be desired.

Table II.

| C. | $\Lambda$. | $\Lambda_0$. |
|---|---|---|
| $1{\cdot}0\times10^{-4}$ | 129·07 | 130·02 |
| $2{\cdot}0\times10^{-4}$ | 128·77 | 130·07 |
| $5{\cdot}0\times10^{-4}$ | 128·11 | 130·08 |
| $1{\cdot}0\times10^{-3}$ | 127·34 | 130·04 |
| $2{\cdot}0\times10^{-3}$ | 126·31 | 130·00 |
| $5{\cdot}0\times10^{-3}$ | 124·41 | 130·00 |
| $1{\cdot}0\times10^{-2}$ | 122·43 | 130·07 |

Fig. 2 shows a selection of the straight lines obtained for electrolytes of different types as described in detail for potassium chloride solution.

In Table III. below are shown the results of these computations for thirty-seven salts of different types *. The

* The conductivity data employed in these calculations were obtained from the following sources :—

Kohlrausch and Maltby, *Wiss. Abh. Techn. Reichsanstalt*, iii. p. 156 (1900) ; *Ges Abh.* ii. p. 826 (1911),
for KCl, NaCl, LiCl, $KNO_3$, $NaNO_3$, and $LiNO_3$.

Kohlrausch, *Berl. Ber.* 1900, p. 1002 ; *Ges. Abh.* ii. p. 942 (1911),
for $KIO_3$, $NaIO_3$, and $LiIO_3$.

Kohlrausch and Steinwehr, *Berl. Ber.* 1902, p. 581 ; *Ges. Abh.* ii. p. 979 (1911), Gruneisen and Steinwehr, *Ges. Abh.* ii. p. 1223 (1911),
for KBr, KI, KF, NaF, $TlNO_3$, TlCl, KCNS, CsCl, $AgNO_3$, and $KClO_3$.

Kohlrausch and Grunëisen, *Berl. Ber.* 1904, p. 1215 ; *Ges. Abh.* ii. p. 1078 (1911), Gruneisen and Steinwehr. *loc. cit.*,
for $Ca(NO_3)_2$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, $Pb(NO_3)_2$, $CaCl_2$, $MgCl_2$, $K_2SO_4$ and $K_2C_2O_4$.

Kendall, J. Chem. Soc. ci. p. 1275 (1912) ; *Medd. K. Vetens. Nobelinstitut*, Bd. ii. no. 38 (1913),
for potassium dichloracetate, potassium trichloracetate, sodiumtrichlorbutyrate, sodium *ortho* nitrobenzoate, sodium cyanacetate, sodium 3 : 5 dinitrobenzoate, and sodium *ortho* chlorobenzoate.

values of $\Lambda_0$ obtained from each value of the concentration are set out in detail, as the constancy of these values over a given range of concentration forms an important feature of the investigation.

Fig. 2.

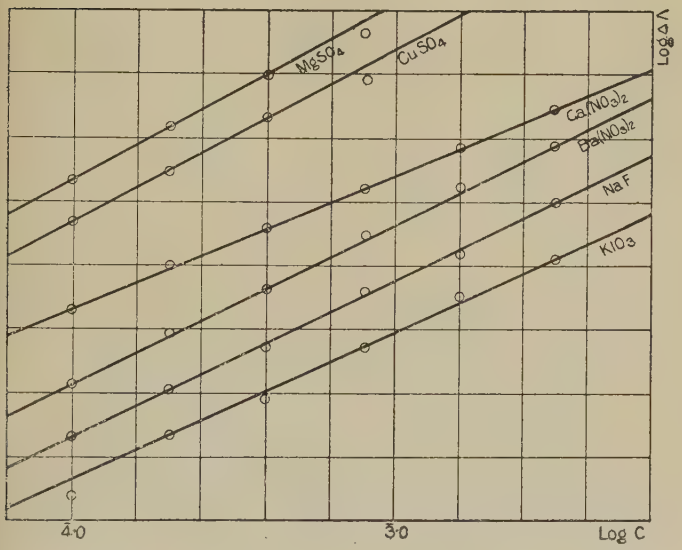



TABLE III.

Uni-univalent Electrolytes. 18° C.

| Concentration. | KCl. $\Lambda_0$. | NaCl. $\Lambda_0$. | LiCl. $\Lambda_0$. | $KNO_3$. $\Lambda_0$. | $NaNO_3$. $\Lambda_0$. | $LiNO_3$. $\Lambda_0$. |
|---|---|---|---|---|---|---|
| $1{\cdot}0\times10^{-4}$ | 130·02 | 109·02 | 99·07 | 126·40 | 105·49 | 95·41 |
| $2{\cdot}0\times10^{-4}$ | 130·07 | 109·06 | 99·11 | 126·44 | 105·48 | 95·43 |
| $5{\cdot}0\times10^{-4}$ | 130·08 | 109·05 | 99·07 | 126·39 | 105·47 | 95·41 |
| $1{\cdot}0\times10^{-3}$ | 130·04 | 109·03 | 99·06 | 126·37 | 105·49 | 95·41 |
| $2{\cdot}0\times10^{-3}$ | 130·00 | 109·00 | 99·03 | 126·39 | 105·49 | 95·38 |
| $5{\cdot}0\times10^{-3}$ | 130·00 | 108·96 | 99·05 | 126·35 | 105·47 | 95·37 |
| $1{\cdot}0\times10^{-2}$ | 130·07 | 109·00 | 99·08 | 126·39 | 105·52 | 95·37 |

TABLE III. (*continued*).

| Concentration. | $KIO_3$. $\Lambda_0$. | $NaIO_3$. $\Lambda_0$. | $LiIO_3$. $\Lambda_0$. | KBr. $\Lambda_0$. | KI. $\Lambda_0$. | KF. $\Lambda_0$. |
|---|---|---|---|---|---|---|
| $1{\cdot}0\times10^{-4}$ | 98·52 | 77·52 | 67·48 | 132·23 | 130·63 | 111·44 |
| $2{\cdot}0\times10^{-4}$ | 98·55 | 77·57 | 67·55 | 132·32 | 130·67 | 111·54 |
| $5{\cdot}0\times10^{-4}$ | 98·57 | 77·55 | 67·54 | 132·32 | 130·76 | 111·54 |
| $1{\cdot}0\times10^{-3}$ | 98·58 | 77·55 | 67·54 | 132·31 | 130·73 | 111·57 |
| $2{\cdot}0\times10^{-3}$ | 98·53 | 77·49 | 67·52 | 132·28 | 130·62 | 111·55 |
| $5{\cdot}0\times10^{-3}$ | 98·52 | 77·52 | 67·52 | 132·28 | 130·55 | 111·61 |
| $1{\cdot}0\times10^{-2}$ | 98·57 | 77·58 | 67·52 | 132·37 | 130·64 | 111·68 |

| Concentration. | NaF. $\Lambda_0$. | $TlNO_3$. $\Lambda_0$. | TlCl. $\Lambda_0$. | KCNS. $\Lambda_0$. | CsCl. $\Lambda_0$. | $AgNO_3$. $\Lambda_0$. | $KClO_3$. $\Lambda_0$. |
|---|---|---|---|---|---|---|---|
| $1{\cdot}0\times10^{-4}$ | 90·08 | 127·37 | 131·09 | 121·00 | 133·06 | 116·12 | 119·52 |
| $2{\cdot}0\times10^{-4}$ | 90·08 | 127·38 | 131·13 | 121·12 | 133·09 | 116·07 | 119·59 |
| $5{\cdot}0\times10^{-4}$ | 90·08 | 127·39 | 131·09 | 121·11 | 133·11 | 116·15 | 119·60 |
| $1{\cdot}0\times10^{-3}$ | 90·07 | 127·39 | 131·08 | 121·10 | 133·13 | 116·21 | 119·59 |
| $2{\cdot}0\times10^{-3}$ | 90·08 | 127·27 | 131·07 | 121·09 | 133·00 | 116·24 | 119·55 |
| $5{\cdot}0\times10^{-3}$ | 90·09 | 127·37 | 130·94 | 121·29 | 133·01 | 116·26 | 119·57 |
| $1{\cdot}0\times10^{-2}$ | 90·11 | 127·55 | 130·96 | 121·57 | 133·07 | 116·25 | 119·60 |

## Uni-bivalent Electrolytes. 18° C.

| Concentration. | $Ca(NO_3)_2$. $\Lambda_0$. | $Sr(NO_3)_2$. $\Lambda_0$. | $Ba(NO_3)_2$. $\Lambda_0$. | $Pb(NO_3)_2$. $\Lambda_0$. |
|---|---|---|---|---|
| $1{\cdot}0\times10^{-4}$ | 114·02 | 113·53 | 116·89 | 123·29 |
| $2{\cdot}0\times10^{-4}$ | 114·01 | 113·53 | 116·89 | 123·44 |
| $5{\cdot}0\times10^{-4}$ | 114·08 | 113·50 | 116·88 | 123·38 |
| $1{\cdot}0\times10^{-3}$ | 114·04 | 113·45 | 116·83 | 123·38 |
| $2{\cdot}0\times10^{-3}$ | 113·96 | 113·41 | 116·79 | 123·45 |
| $5{\cdot}0\times10^{-3}$ | 113·96 | 113·48 | 116·94 | 123·68 |
| $1{\cdot}0\times10^{-2}$ | 114·10 | 113·80 | 117·58 | 124·07 |

TABLE III. (*continued*).

| Concentration. | $CaCl_2$. $\Lambda_0$. | $MgCl_2$. $\Lambda_0$. | $K_2SO_4$. $\Lambda_0$. | $K_2C_2O_4$. $\Lambda_0$. |
|---|---|---|---|---|
| $1{\cdot}0\times10^{-4}$ | 116·81 | 111·55 | 132·85 | 125·70 |
| $2{\cdot}0\times10^{-4}$ | 116·81 | 111·65 | 132·95 | 125·80 |
| $5{\cdot}0\times10^{-4}$ | 116·79 | 111·72 | 132·89 | 125·70 |
| $1{\cdot}0\times10^{-3}$ | 116·73 | 111·68 | 132·87 | 125·45 |
| $2{\cdot}0\times10^{-3}$ | 116·63 | 111·54 | — | 125·18 |
| $5{\cdot}0\times10^{-3}$ | 116·73 | 111·42 | 132·79 | 125·63 |
| $1{\cdot}0\times10^{-2}$ | 117·16 | 111·49 | 133·01 | 127·17 |

Bi-bivalent Electrolytes. 18° C.

| Concentration. | $MgSO_4$. $\Lambda_0$. | $CuSO_4$. $\Lambda_0$. | $CdSO_4$. $\Lambda_0$. |
|---|---|---|---|
| $1{\cdot}0\times10^{-4}$ | 113·78 | 114·16 | 114·66 |
| $2{\cdot}0\times10^{-4}$ | 113·77 | 114·15 | 114·66 |
| $5{\cdot}0\times10^{-4}$ | 113·68 | 114·09 | 114·63 |
| $1{\cdot}0\times10^{-3}$ | 113·79 | 114·22 | 114·86 |

Uni-univalent Electrolytes. 25° C.

| Concentration. | Potassium dichloracetate. $\Lambda_0$. | Potassium trichloracetate. $\Lambda_0$. | Sodium trichlorbutyrate. $\Lambda_0$. | Sodium *ortho* nitrobenzoate. $\Lambda_0$. |
|---|---|---|---|---|
| $4{\cdot}833\times10^{-4}$ | — | — | — | 83·8 |
| $9{\cdot}766\times10^{-4}$ | 122·6 | 119·0 | 82·3 | 83·8 |
| $1{\cdot}953\times10^{-3}$ | 122·4 | 119·0 | 82·3 | 83·8 |
| $3{\cdot}906\times10^{-3}$ | 122·5 | 119·0 | 82·3 | 83·8 |
| $7{\cdot}813\times10^{-3}$ | 122·4 | 119·3 | 82·3 | 83·8 |
| $1{\cdot}563\times10^{-2}$ | 122·6 | 119·9 | 82·3 | 83·9 |

| Concentration. | Sodium cyanoacetate. $\Lambda_0$. | Sodium 3 : 5 dinitrobenzoate. $\Lambda_0$. | Sodium *ortho* chlorbenzoate. $\Lambda_0$. |
|---|---|---|---|
| $4{\cdot}883\times10^{-4}$ | 92·8 | 79·7 | 86·8 |
| $9{\cdot}766\times10^{-4}$ | 92·9 | 79·7 | 86·8 |
| $1{\cdot}953\times10^{-3}$ | 92·9 | 79·7 | 86·8 |
| $3{\cdot}906\times10^{-3}$ | 92·8 | 79·7 | 86·7 |
| $7{\cdot}813\times10^{-3}$ | 92·8 | 79·8 | 86·4 |
| $1{\cdot}563\times10^{-2}$ | 94·8 | 80·6 | 85·7 |

TABLE IV.

| Substance. | Temperature. | $\Lambda_0$. | B. | *n*. |
|---|---|---|---|---|
| KCl | 18° C. | 130·04 | 61·26 | 0·4520 |
| NaCl | ,, | 109·02 | 54·24 | 0·4431 |
| LiCl | ,, | 99·07 | 51·74 | 0·4364 |
| $KNO_3$ | ,, | 126·39 | 74·67 | 0·4796 |
| $NaNO_3$ | ,, | 105·48 | 57·32 | 0·4458 |
| $LiNO_3$ | ,, | 95·40 | 47·96 | 0·4253 |
| $KIO_3$ | ,, | 98·54 | 61·07 | 0·4604 |
| $NaIO_3$ | ,, | 77·54 | 54·66 | 0·4551 |
| $LiIO_3$ | ,, | 67·53 | 48·22 | 0·4422 |
| KBr | ,, | 132·30 | 58·15 | 0·4324 |
| KI | ,, | 130·66 | 60·86 | 0·4636 |
| KF | ,, | 111·54 | 56·34 | 0·4409 |
| NaF | ,, | 90·08 | 62·69 | 0·4831 |
| $TlNO_3$ | ,, | 127·39 | 113·10 | 0·5458 |
| TlCl | ,, | 131·04 | 152·73 | 0·5763 |
| KCNS | ,, | 121·08 | 74·35 | 0·4947 |
| CsCl | ,, | 133·07 | 80·97 | 0·5062 |
| $AgNO_3$ | ,, | 116·19 | 64·17 | 0·4404 |
| $KClO_3$ | ,, | 119·57 | 70·86 | 0·4747 |
| $Ca(NO_3)_2$ | ,, | 114·02 | 100·63 | 0·4196 |
| $Sr(NO_3)_2$ | ,, | 113·49 | 121·72 | 0·4582 |
| $Ba(NO_3)_2$ | ,, | 116·87 | 175·63 | 0·5120 |
| $Pb(NO_3)_2$ | ,, | 123·44 | 164·50 | 0·4520 |
| $CaCl_2$ | ,, | 116·75 | 115·84 | 0·4622 |
| $MgCl_2$ | ,, | 111·63 | 83·87 | 0·3991 |
| $K_2SO_4$ | ,, | 132·85 | 141·98 | 0·4582 |
| $K_2C_2O_4$ | ,, | 125·73 | 323·97 | 0·6772 |
| $MgSO_4$ | ,, | 113·72 | 626·2 | 0·5507 |
| $CuSO_4$ | ,, | 114·16 | 810·2 | 0·5711 |
| $CdSO_4$ | ,, | 114·70 | 771·5 | 0·5511 |
| Potassium dichloracetate | 25° C. | 122·5 | 44·75 | 0·1707 |
| Potassium trichloracetate | ,, | 119·0 | 56·96 | 0·2240 |
| Sodium trichlorbutyrate | ,, | 82·3 | 34·64 | 0·2689 |
| Sodium *ortho* nitrobenzoate | ,, | 83·8 | 54·23 | 0·4000 |
| Sodium cyanacetate | ,, | 92·9 | 35·85 | 0·2605 |
| Sodium 3 : 5 dinitrobenzoate | ,, | 79·7 | 70·27 | 0·4862 |
| Sodium *ortho* chlorbenzoate | ,, | 86·8 | 31·62 | 0·2413 |

It should be noted that the values of $\Lambda_0$ thus calculated from equation (2) are in all instances as consistent with each other as the experimental figures will permit. Thus, for potassium chloride, over a range of concentration 0·0001 N to 0·01 N, the value of $\Lambda_0$ nowhere differs from the mean value by more than four parts in thirteen thousand, that is by about 0·03 per cent., and the order of the error is about the same for the first nine salts given in Table III., these salts being precisely the ones which have been subject to the most careful experimental investigation. A conspectus of the whole series of results giving the values of B, $n$, and the mean values of $\Lambda_0$ is exhibited in Table IV.

The mean values of $\Lambda_0$ thus obtained for the first nine electrolytes given in Table IV. are in fairly good agreement with those of Kohlrausch, although in extreme cases the deviations may be as much as 0·2 per cent. In the case of the other electrolytes the deviations are sometimes greater. Kohlrausch has used several formulæ for the computation of $\Lambda_0$, in particular

$$\Lambda_0 = \Lambda + \mathrm{P}C^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\Lambda_0 = \Lambda + k\Lambda^p C^{\frac{1}{2}} . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The values of $\Lambda_0$ obtained from these equations are shown for several instances in Table V. below. For convenience of comparison the values of $\Lambda_0$ obtained from equation (2) are appended. It will be seen that while equations (7) and (2) give results which are very self consistent, the values of $\Lambda_0$ obtained from equation (8) fall off slightly with increasing dilution. This deviation becomes more pronounced as the valency of the electrolyte increases, and it seems safe to conclude that equation (8) should not be used for the computation of the limiting conductivities of uni-bivalent, bi-bivalent, and higher types of electrolytes *.

Inspection of Table IV. makes apparent certain regularities which may here be noted. For elements belonging to the same group in the Periodic Table, the values of B and $n$ increase regularly with increasing atomic weight. It is not possible, considering the fewness of the points, to postulate with certainty any quantitative law, but if we assume that, within the limits considered, B and $n$ are linear functions of the atomic weight, the results exhibited in Table VI. are obtained.

* Compare also Kohlrausch, *Ges. Abh.* ii. p. 1136 (1911).

TABLE V.

| Substance. | $\Lambda_0=\Lambda+PC^{\frac{1}{2}}$. | $\Lambda_0=\Lambda+k\Lambda_0^{p}C^{\frac{1}{2}}$. | $\Lambda_0=\Lambda+BC^{n}$. | Concentration. |
|---|---|---|---|---|
| KCl ..... | 129·88 | 129·98 | 130·02 | $1·0\ 10^{-4}$ |
| | 129·91 | 130·05 | 130·07 | $2·0\times10^{-4}$ |
| | 129·94 | 130·10 | 130·08 | $5·0\times10^{-4}$ |
| | 129·91 | 130·10 | 130·04 | $1·0\times10^{-3}$ |
| NaCl ..... | 108·85 | 108·92 | 109·02 | $1·0\times10^{-4}$ |
| | 108·87 | 108·97 | 109·06 | $2·0\times10^{-4}$ |
| | 108·87 | 108·98 | 109·05 | $5·0\times10^{-4}$ |
| | 108·86 | 108·99 | 109·03 | $1·0\times10^{-3}$ |
| $KClO_3$ ..... | Not | 119·55 | 119·52 | $1·0\times10^{-4}$ |
| | calculated | 119·63 | 119·59 | $2·0\times10^{-4}$ |
| | by | 119·67 | 119·60 | $5·0\times10^{-4}$ |
| | Kohlrausch. | 119·69 | 119·59 | $1·0\times10^{-3}$ |
| CsCl..... | Not | 133·3 | 133·06 | $1·0\times10^{-4}$ |
| | calculated | 133·2 | 133·09 | $2·0\times10^{-4}$ |
| | by | 133·51 | 133·11 | $5·0\times10^{-4}$ |
| | Kohlrausch. | 133·63 | 133·13 | $1·0\times10^{-3}$ |
| $Ba(NO_3)_2$... | 116·99 | 117·29 | 116·89 | $1·0\times10^{-4}$ |
| | 117·01 | 117·43 | 116·89 | $2·0\times10^{-4}$ |
| | 117·03 | 117·63 | 116·88 | $5·0\times10^{-4}$ |
| | 116·99 | 117·73 | 116·83 | $1·0\times10^{-3}$ |
| $K_2SO_4$ .. ... | 132·53 | 133·04 | 132·85 | $1·0\times10^{-4}$ |
| | 132·59 | 133·24 | 132·95 | $2·0\times10^{-4}$ |
| | 132·54 | 133·39 | 132·95 | $5·0\times10^{-4}$ |
| | 132·54 | 133·55 | 132·95 | $1·0\times10^{-3}$ |
| $K_2C_2O_4$ ... | — | 127·19 | 125·70 | $1·0\times10^{-4}$ |
| | 127·05 | 127·71 | 125·80 | $2·0\times10^{-4}$ |
| | 127·29 | 128·20 | 125·70 | $5·0\times10^{-4}$ |
| | 127·32 | 128·43 | 125·45 | $1·0\times10^{-3}$ |

It is of interest to test the consistency of the values of $\Lambda_0$ obtained by different methods by an application of Kohlrausch's law of independent migration of ions, which states that the differences between the mobilities of any two ions at infinite dilution is independent of the particular salts from which it is determined; for at infinite dilution we have obviously

$$_{KX}\Lambda_0-{}_{KY}\Lambda_0=C(U_X-U_Y),$$

TABLE VI.

| | Atomic Weight. | B. | * B calcd. | $n$. | * $n$ calcd. |
|---|---|---|---|---|---|
| Chlorides of | | | | | |
| Li ..... | 6·94 | 51·74 | 51·74 | 0·4364 | 0·4366 |
| Na ..... | 23·00 | 54·24 | 55·70 | 0·4431 | 0·4452 |
| K ..... | 39·10 | 61·26 | 59·94 | 0·4520 | 0·4539 |
| Cs ..... | 132·81 | 80·97 | 80·97 | 0·5062 | 0·5058 |
| Nitrates of | | | | | |
| Li ..... | 6·94 | 47·96 | 47·96 | 0·4253 | 0·4253 |
| Na ..... | 23·00 | 57·32 | 62·35 | 0·4458 | 0·4522 |
| K ..... | 39·10 | 74·67 | 74·67 | 0·4796 | 0·4796 |
| Iodates of | | | | | |
| Li ..... | 6·94 | 48·22 | 48·22 | 0·4422 | 0·4422 |
| Na ..... | 23·00 | 54·66 | 54·66 | 0·4551 | 0·4512 |
| K ..... | 39·10 | 61·07 | 61·07 | 0·4604 | 0·4604 |
| Nitrates of | | | | | |
| Ca ..... | 40·07 | 100·63 | 100·63 | 0·4196 | 0·4196 |
| Sr ..... | 87·63 | 121·72 | 137·05 | 0·4582 | 0·4643 |
| Ba ..... | 137·37 | 175·63 | 175 63 | 0·5120 | 0·5120 |

* These values are derived from the plots of B and $n$ against the atomic weight W. These plots are all as nearly as possible linear, of the form $B = p+qW$, $n = p'+q'W$.

TABLE VII.

| | Authors. | Kohlrausch and Maltby "Schlusswerte." | Kohlrausch $\Lambda_0$ from $\Lambda_0 = \Lambda + k\Lambda^p C^{\frac{1}{2}}$. |
|---|---|---|---|
| $NaCl$–$NaNO_3$... | 3·54 | 3·57 | 3·66 |
| $KCl$–$KNO_3$..... | 3·65 | 3·51 | 3·60 |
| $LiCl$–$LiNO_3$ ... | 3·67 | 3·71 | 3·70 |
| Mean..... | 3·62 | 3·60 | 3·65 |
| $KCl$–$NaCl$ ..... | 21·02 | 21·04 | 21·11 |
| $KNO_3$–$NaNO_3$ . | 20·91 | 21·10 | 21·17 |
| $KIO_3$–$NaIO_3$ ... | 21·00 | — | 21·07 |
| Mean..... | 20·98 | 21·07 | 21·12 |
| $KCl$–$LiCl$ ..... | 30·97 | 31·02 | 31·22 |
| $KNO_3$–$LiNO_3$ . | 30·99 | 31·22 | 31·32 |
| $KIO_3$–$LiIO_3$ ... | 31·01 | — | 31·13 |
| Mean..... | 30·99 | 31·11 | 31·22 |
| $NaCl$–$NaIO_3$ ... | 31·48 | — | 31·57 |
| $KCl$–$KIO_3$..... | 31·50 | — | 31·61 |
| $LiCl$–$LiIO_3$ ... | 31·54 | — | 31·52 |
| Mean..... | 31·51 | — | 31·57 |

and independent of the nature of the cation. The results are presented in Table VII., and for the sake of comparison calculations based on Kohlrausch's $\Lambda_0$ values are appended.

It will be seen that the differences obtained are in close agreement with each other and with the mean values deduced from Kohlrausch's values for $\Lambda_0$. Indeed, on the whole, the variations from the mean in column 1 are markedly less than the corresponding variations in columns 2 and 3.

TABLE VIII.

| Cations. 18° C. | | Anions. 18° C. | |
|---|---|---|---|
| Ion. | $\Lambda_{0c+}$. | Ion. | $\Lambda_{0a-}$. |
| $K^+$ | 64·60 | $Cl^-$ | 65·54 |
| $Na^+$ | 43·48 | $NO_3^-$ | 61·83 |
| $Li^+$ | 33·53 | $IO_3^-$ | 34·00 |
| $Tl^+$ | 65·53 | $Br^-$ | 67·70 |
| $Cs^+$ | 67·53 | $I^-$ | 66·06 |
| $Ag^+$ | 54·36 | $F^-$ | 46·77 |
| $\frac{1}{2}Ca^{++}$ | 52·19 | $CNS^-$ | 56·48 |
| $\frac{1}{2}Sr^{++}$ | 51 66 | $ClO_3^-$ | 54·97 |
| $\frac{1}{2}Ba^{++}$ | 55·04 | $\frac{1}{2}SO_4^{--}$ | 68·25 |
| $\frac{1}{2}Pb^{++}$ | 61·61 | $\frac{1}{2}C_2O_4^{--}$ | 61·13 |
| $\frac{1}{2}Mg^{++}$ | 45·78 | | |
| $\frac{1}{2}Cd^{++}$ | 46·45 | | |
| $\frac{1}{2}Cu^{++}$ | 45·91 | | |

| Anions. 25° C. | |
|---|---|
| Ion. | $\Lambda_{0a-}$. |
| Dichloracetate$^-$ | 57·9 |
| Trichloracetate$^-$ | 54·4 |
| Trichlorbutyrate$^-$ | 38·8 |
| *Ortho* nitrobenzoate$^-$ | 40·3 |
| Cyanacetate$^-$ | 49·4 |
| 3 : 5 dinitrobenzoate$^-$ | 36·2 |
| *Ortho* chlorbenzoate$^-$ | 43·3 |

The ionic conductivities based on the $\Lambda_0$ values given in Table IV. and on the figure 0·5040 as the anion transference

number for potassium chloride * have been calculated, and are collected in Table VIII.

The authors hope in the near future to employ the values thus obtained in a discussion of certain other dilution formulæ.

East London College
(University of London),
June 1925.

---

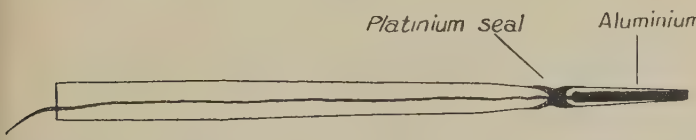
CVI. *The Generation of Oscillations by a Discharge-Tube.* *By* R. E. Clay, *A.R.C.S., B.Sc.(Lond.), M.Sc.(Cantab.)* †.

THE generation of oscillations by a discharge-tube is now a well-known phenomenon. Several types of oscillation are set up under different conditions, and a study of the variation of frequency with gas-pressure, current, and capacity shows that the mechanism of their generation is different. The following paper deals with oscillations set up in tubes of special design which will be described.

Several tubes were made, but of those which worked in the manner here under consideration, small changes in the dimensions had little or no effect on the results obtained ; it will therefore suffice to describe one tube which may be taken as typical.

The anode (fig. 1) was made by drawing down a piece of

Fig. 1.




quill tubing to a slow taper; this was cut at the point where a piece of aluminium wire about 2 mm. in diameter just fitted it.

A piece of this aluminium wire about 3 cm. long was joined to a short piece of platinum wire, to the other end of which was joined a copper lead ; a bead of sealing-in glass was fused on to the centre of the platinum, and the whole was then pushed into the quill tube so that the aluminium just protruded.

* Compare Noyes and Falk, J. Amer. Chem. Soc. xxxiii. p. 1436 (1911) ; Washburn, *ibid.* xl. p. 150 (1918).

† Communicated by Sir J. J. Thomson, O.M., F.R.S.

By warming the tube opposite the bead so that it collapsed and fused onto the bead, an air-tight seal was made; the aluminium and the end of the glass tube were then ground off flush, and cleaned by boiling in dilute nitric acid and in several changes of distilled water.

A piece of quill tubing into which the anode was an easy fit was chosen, and was joined to a piece of tube about 2 cm. in diameter; on the end of this a bulb 5 cm. in diameter was blown. A short piece of platinum wire was sealed through the bulb at one point, and the inner surface was then silvered with a chemical solution; this coat of silver formed the cathode. The end of the anode, that is to say the exposed cross-section of the aluminium wire, was arranged at the centre of the bulb, and was thus entirely surrounded by the cathode. A small window for observing the appearance of the discharge was scratched in the silver with a bent wire.

The gases used in these experiments were mainly air and hydrogen; a few observations were made in helium.

The air was dried over phosphorus pentoxide, and was admitted to the discharge-tube through a trap in liquid air; this ensured that it was dry and also removed the vapours of mercury and tap-grease.

The hydrogen was generated by the electrolysis of dilute sulphuric acid; it was purified by passing it through strong pure sulphuric acid, then over potash and phosphorus pentoxide, and finally standing over charcoal in liquid air.

The helium was freed from hydrogen by burning phosphorus in it with excess of oxygen; the oxygen and other impurities were then removed by standing over charcoal in liquid air.

A Gaede mercury pump was used for exhaustion, and the pressure was measured with a McLeod gauge.

Current for the discharge was obtained from a battery of 500 small accumulators; it was passed through the filament-anode space of an R valve of which the filament current was adjusted by a rheostat *. Oscillations of the type first under consideration were set up when the filament current was so adjusted that the valve allowed a current of the order of 1 milliampere to pass through the discharge-tube.

The discharge was then concentrated in a very bright spot in the centre of the anode, which was red in the case of air and blue in the case of hydrogen; this was surrounded by a faint glow of the same colour. The appearance did not alter very much over the ranges of pressure and current for

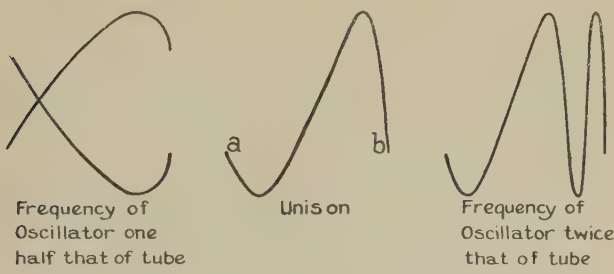
* This very convenient method of adjusting the current was suggested by Dr. Appleton.

which the discharge took this form, though increase of current or decrease of pressure caused the bright spot to become even brighter.

The frequency was measured with a heterodyne oscillator in conjunction with a cathode-ray oscillograph. One of the two pairs of deflecting plates of the oscillograph was connected across a resistance of $10^5$ ohms which was in series with the discharge-tube; the deflexion obtained was thus proportional to the current through this resistance. The other pair of deflecting plates was connected to the valve oscillator or heterodyne.

For each frequency of the oscillator giving a combination tone in the telephones, a Lissajous figure appeared on the oscillograph screen; the shape of the figure for several ratios of the frequencies of the tube and the oscillator is shown in fig. 2.

Fig. 2.




Deflexion in a horizontal direction is due to the discharge-tube, and in a vertical direction to the heterodyne oscillator.

Consider the curve obtained at unison: it is evident that we must assume that a jump occurs between the points $a$ and $b$, the spot traversing the screen so fast that luminescence of the Willemite is not excited. For since the vertical motion is approximately simple harmonic, the spot cannot retrace the curved path on reaching the end, as this would involve an abrupt change in the phase of the harmonic motion.

Since the curve is steeper at $b$ than at $a$, the horizontal motion when the curve is traced is accelerated from $b$ to $a$; the curve does not, however, give any information concerning the sense of the velocity.

On several occasions, however, when the tube was running particularly steadily, it was possible to raise (say) the frequency of the oscillator very slightly above that of the tube; the phase relationship between the two systems of oscillations

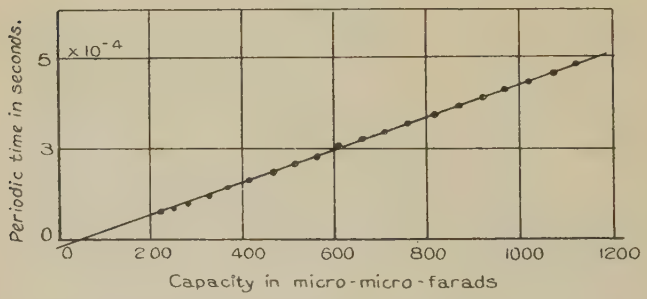
then went through a cyclic change a few times a second, and it was possible to notice whether the line *ab* moved up or down the figure; it was found to move *down* when the frequency of the oscillator was *above* that of the tube.

This indicates that the jump is from *b* to *a*, for the phase of the vertical motion at the instant when the jump occurs must be a little later each time.

When the current through the resistance is increased, the spot moves from *b* to *a*. The current therefore rises very suddenly and then falls off, rapidly at first, but less and less rapidly till the next sudden rise occurs.

If a variable condenser is connected with the discharge-tube, it is found that the reciprocal of the frequency, that is to say the periodic time, is proportional to the capacity; this is shown in fig. 3, in which the periodic time is plotted as

Fig. 3.




ordinates against the reading in micro-microfarads of a small variable air condenser as abscissæ. By connecting a condenser of about one-tenth of a microfarad across the tube, the frequency could be reduced to one flash in several seconds. The energy passing at each discharge under these conditions was excessive, and rapidly damaged the electrodes if allowed to continue.

The action would appear to be as follows :—The condenser in parallel with the discharge-tube is charged up through the high resistance in series (chiefly the filament-plate space of the valve; the shape of the wave is probably determined largely by the peculiar properties of this resistance), the current dying down approximately exponentially; when the potential difference reaches a certain value, a sudden discharge occurs and the potential of the condenser falls, the current through the resistance rises suddenly, and the condenser once more commences to charge up.

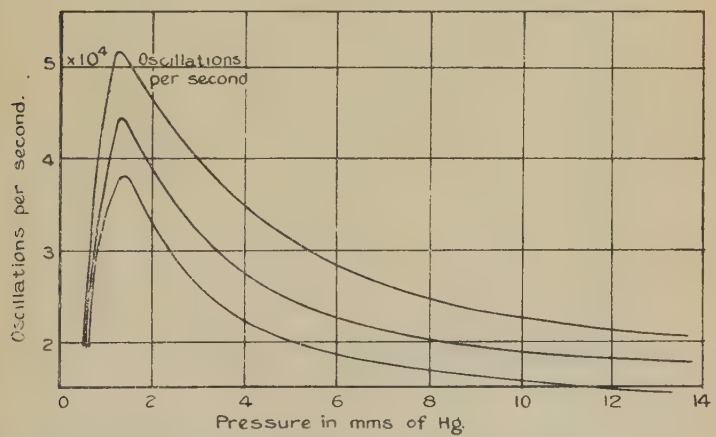
This action is identical with that of the Neon lamp.

Although the voltage across the discharge-tube was not measured directly, it is possible to calculate this as follows:—

If $c$ is the capacity of the discharge-tube and condenser, $i$ the mean current, and $t$ the periodic time, then the voltage V across the discharge-tube at the instant when a discharge occurs may be shown to be $V = it/c$, on the assumption that the decay of the current is exponential.

The relation between frequency and gas-pressure when hydrogen was used is shown for three values of the mean current in fig. 4; from these curves it is of interest to

Fig. 4.



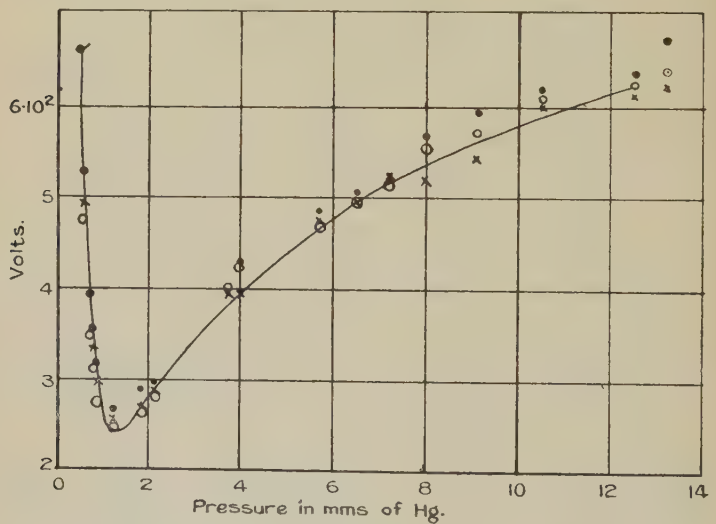

calculate, in the way indicated above, the voltage at which the discharge occurs for each value of the pressure. The curve in fig. 5 is plotted in this way, and it will be noticed that the three sets of points (shown on the graph by different kinds of marks) lie very well on the same curve, showing that the voltage at which the discharge occurs is independent of the mean current.

The results obtained in air were of the same general nature as those described above; with the same current as in hydrogen, the maximum frequency occurred at about half the pressure and had about half the value.

If the saturation current of the R valve in series with the discharge-tube is reduced to 100 microamperes, the discharge takes an entirely different form, and sets up oscillations whose properties differ in several important respects from those described in the first part of this paper. If the tube is filled with hydrogen at a pressure of 10 mm. of mercury,

a faint blue glow on the surface of the anode is visible ; if the pressure is now gradually reduced, this glow becomes brighter and a fainter glow surrounding it becomes visible ; a slight increase in the size of the inner glow now takes place, the outer glow remaining almost unchanged. At a pressure of about 5 mm. the inner glow suddenly swells out and fills the outer faint glow ; it is now joined to the anode by a narrow neck only. As the pressure is further reduced, the whole appearance enlarges and becomes mushroom-shaped. This form of discharge persists down to a pressure of about 2 mm.

Fig. 5.




Oscillations of much smaller amplitude are set up by this mushroom-shaped discharge, and since the sensitivity of the oscillograph was insufficient, other means had to be adopted to obtain the fundamental frequency. In an appendix to this paper it is shown that when both the system whose frequency is required and a heterodyne are generating strong harmonics, it is not possible directly to determine with certainty the fundamental of the unknown system.

The second method described in the appendix was used.

The family of curves shown in fig. 6 was obtained by observing the frequency as the current was varied, the pressure remaining constant at the values marked on the figure. The variation of frequency with pressure at constant current is shown in fig. 7 for three different discharge-tubes, the current being 100 microamperes in each case. Curve *a* is for a

Fig. 6.

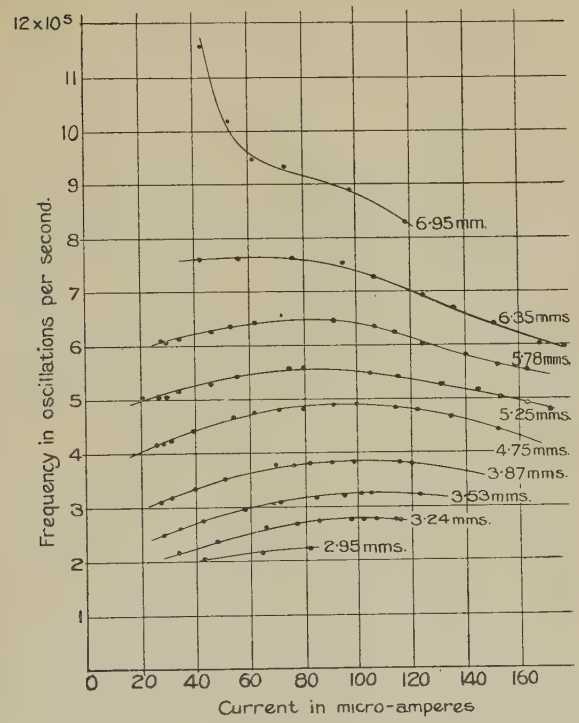
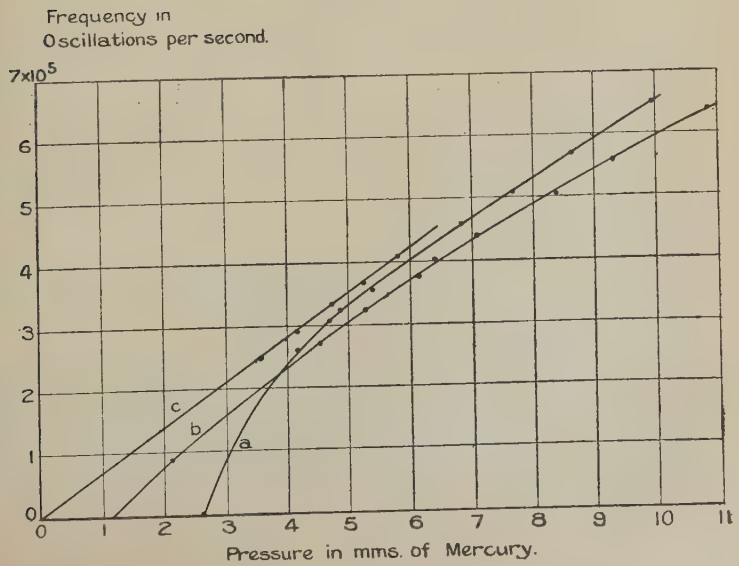

12x10⁵
11
10
9
8
7
6
5
4
3
2
1
Frequency in oscillations per second.
6·95mm.
6·35mms.
5·78mms.
5·25mms.
4·75mms.
3·87mms.
3·53mms.
3·24mms.
2·95mms.
0
20
40
60
80
100
120
140
160
Current in micro-amperes

Fig. 7.


Frequency in
Oscillations per second.
7x10⁵
6
5
4
3
2
1
0
c
b
a
0
1
2
3
4
5
6
7
8
9
10
11
Pressure in mms. of Mercury.

tube of which the spherical cathode was 6·5 cm. in diameter and the anode a disk of aluminium 1·72 mm. in diameter, *b* is for a bulb 5·3 cm. in diameter and an anode 1·78 mm. in diameter, and *c* is for a bulb 5·1 cm. in diameter and an anode 2 mm. in diameter.

The purity of the hydrogen is an important factor; although the gas was allowed to stand over charcoal in liquid air, the spectrum always showed traces of oxygen and nitrogen, and the liquid-air trap next to the discharge-tube always collected a solid deposit which evaporated off when the liquid air was removed—this probably consisted of tap-grease and other hydrocarbons.

If the liquid air were removed from the trap while the discharge was running, the appearance at once changed and the oscillations ceased. Even with the trap in liquid air, it was only occasionally that the oscillations were generated sufficiently steadily for readings to be taken.

Unless the surface of the anode was very clean, the discharge would not take the required form, but concentrated itself in very small and very bright points of light. If the discharge were allowed to run in this condition, the anode became pitted and had to be removed and reground before it could be made to work as required

It was cleaned after grinding by boiling in dilute nitric acid followed by several changes of distilled water, and, after mounting it in the discharge-tube, it was run as a cathode with a current of several milliamperes until any small red spots disappeared and all flickering ceased.

It was not possible to obtain a discharge of this nature in air, but in helium it was more easily obtained than in hydrogen, although in this gas small traces of impurity had a much greater effect upon the frequency. The helium was spectroscopically very pure, and was admitted to the discharge-tube through a trap in liquid air, the tube itself having been previously thoroughly exhausted with charcoal and liquid air while gently warmed—the presence of wax joints rendered baking impossible.

The frequencies of all the oscillations found in helium were much lower than in hydrogen, and the ranges of pressure and current over which the oscillations were produced were much wider.

If the pressure was kept constant and the current gradually increased, the appearance of the discharge went through a somewhat more complex series of changes than was the case in hydrogen. Sudden changes occurred which were accompanied by sudden changes in the frequency, and,

though these would repeat if the current was reduced and again gradually increased, they did not occur in the reverse order as the current was gradually reduced: a different series of changes took place.

The complexity of the behaviour in helium has not been satisfactorily unravelled nor the results obtained reduced to order, and for this reason curves are not shown. It is remarkable that the frequency falls as the pressure increases instead of rising as in the case in hydrogen, and that a small trace of oxygen causes a great change in the behaviour, the frequency now rising as the pressure increases.

The chief peculiarity of these oscillations, which differentiates them from those described in the earlier part of this paper, is that a capacity connected in parallel with the discharge-tube has no effect on the frequency, though it appears somewhat to diminish the amplitude of the oscillations.

*Summary.*

The paper deals with oscillations generated by two types of discharge that occur in discharge-tubes in which the anode is a small disk of aluminium situated at the centre of a spherical silver cathode.

The current through the tube in the case of one of the types of discharge is analysed with a cathode-ray oscillograph, and a theory is given of the action. The current is weaker in the second case, and the frequency had to be obtained by a heterodyne method.

Whereas the frequency in the first case is dependent on the electrical capacity of the discharge-tube, in the second type of discharge the frequency is quite independent of this factor.

The discharge can only be made to pass in the second form when the gas is very pure and the frequency is very sensitive to a trace of impurity.

## Appendix.

### *The Determination of the Frequency of Electrical Oscillations when Harmonics are present.*

The frequency of sustained electrical oscillations is very conveniently determined by the heterodyne method. Oscillations are generated in a closed circuit by means of a triode valve; this circuit is loosely coupled to the system of which the frequency is required, and the frequency of the heterodyne oscillations is varied until the combination tone due

to approximate coincidence of harmonics of the two systems is heard in a telephone connected in the plate circuit of the valve. When the pitch of the combination tone is zero, the harmonics are exactly in tune.

If $a$ is the fundamental frequency of the unknown system, and $b$ the variable fundamental frequency of the heterodyne, and if they are accompanied by the harmonics

$$2a,\ 3a,\ 4a,\ \ldots\ldots\ na$$

and $2b,\ 3b,\ 4b,\ \ldots\ldots\ mb$ respectively, then the condition for zero pitch of the combination tone is

$$na = mb.$$

In this equation $b$ only is known, so that it is impossible from it to determine $a$.

By altering the adjustments several values can be found for $b$, in which different harmonics of both systems are involved, and for each of which the pitch of the difference tone is zero.

For each of these values a relation of the above form holds; *i. e.*,

$$n_1 a = m_1 b_1,$$

$$n_2 a = m_2 b_2,$$

$$\ldots\ldots\ldots$$

But, again, only the $b$'s are known, the $m$'s and $n$'s can have any integral values, and it is not possible to determine $a$.

Further information is supplied by finding what may be termed the "width" of a combination tone. As the frequency of the heterodyne is varied continuously through a value for which a combination tone is heard, its pitch comes down from above the audible limit, falls to zero, and then rises above the audible limit once more. Let $\Delta b$ be the change in $b$ required to change the pitch of the combination tone from zero to a value $f$; this may be defined as half the width of the combination tone.

When the pitch of the combination tone is $f$, we have

$$na = m(b + \Delta b) - f;$$

but $$na = mb.$$

Hence

$$m = \frac{f}{\Delta b}.$$

So that we can find the harmonic of the heterodyne that is concerned.

By repeating this procedure with several of the pairs of harmonics, we find a series of values $n_1a$, $n_2a$, $n_3a$, . . . . . , in which, of course, the $n$'s are integers.

The value of $a$ is then most easily found by the aid of a slide-rule ; the values $n_1a$, $n_2a$, $n_3a$, . . . . . are marked with small dots of ink on the D scale of the rule, and the slider is then adjusted until a series of integers on the C scale coincides as closely as possible with the ink marks; the reading on the D scale opposite 1 on the C scale then gives the value of $a$.

A second method was developed in which the direct coupling between the unknown circuit and the heterodyne is reduced by separating them to a distance of several feet.

A resonance circuit is connected in series with a small coil coupled to the unknown circuit ; the oscillations in this circuit are then investigated with the heteroydne.

Resonance is very sharp and the oscillations set up are very pure, so that it is easy to pick out one harmonic of the unknown circuit at a time, and to determine its frequency by finding several values of $b$ for which a combination tone has zero pitch.

If these values are $b_1$, $b_2$, $b_3$, as before, we have

$$m_1b_1 = m_2b_2 = m_3b_3 = n_1a.$$

The values of $b_1$, $b_2$, $b_3$ are marked with a pen on the A scale of a slide-rule opposite the appropriate readings on the D scale ; the slider is removed and replaced inverted so that the C scale can be adjusted until a series of integers on it coincides as closely as possible with the marks; the reading on the D scale opposite the 1 on the slider is then the value of $n_1a$.

This is repeated for several harmonics of the unknown system and values found for $n_1a$, $n_2a$, $n_3a$, . . . . . , from which the value of $a$ can be found with the use of the slide-rule as before.

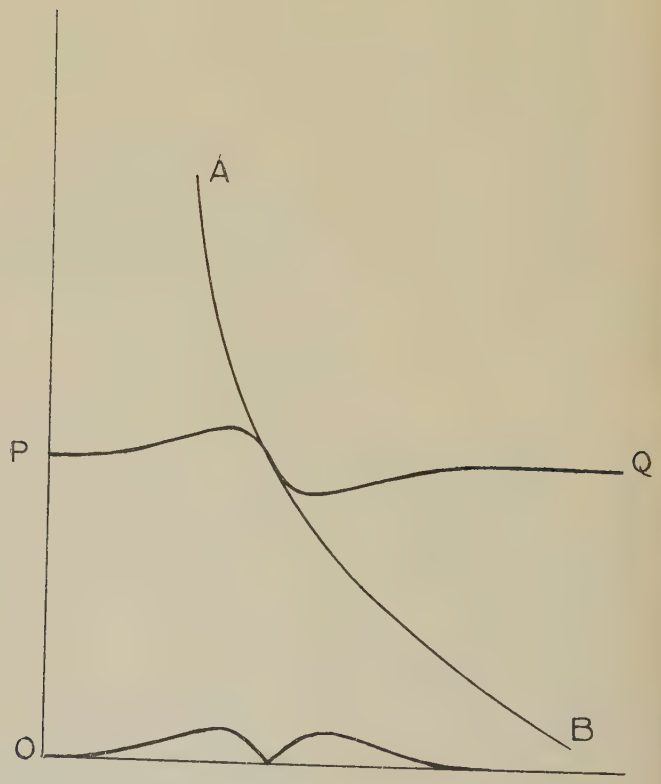
The process is less tedious than it sounds, as it is usually found that the ink marks on the slide-rule fit integers without any ambiguity, and three or four marks are sufficient to determine the position of the slider uniquely.

The resonance circuit forces the unknown circuit a little out of its natural frequency when it is not quite in tune. This, however, is rather an advantage than otherwise.

Let AB (fig. 8) represent the relation between the natural frequency of the resonance circuit and its adjustment scale ; and let OP be the natural frequency of the unknown system.

When the free frequency of the resonance circuit is greatly different from that of the unknown system, oscillations in the resonance circuit are entirely forced at the frequency of the unknown system. When, however, the free frequency of the resonance circuit approaches that of the unknown system, the amplitude of the oscillations in the

Fig. 8.




resonance circuit increases, and this circuit reacts upon the unknown system, forcing it out of its natural frequency. In this way we may expect a curve of the form PQ to represent the relation between the frequency of the oscillations induced in the resonance circuit and its adjustment scale.

If, now, these oscillations are heterodyned by an oscillator whose frequency is OP, the combination tone will rise to

two maxima separated by a sharp fall to zero pitch. The two maxima will have the same pitch only when the frequency of the heterodyne oscillator is the same as the natural frequency of the unknown system. Thus an accurate setting of the heterodyne can be made by adjusting it until, on moving the condenser of the resonance circuit through the resonance point, the two maxima are of equal strength.

*Summary of Appendix.*

It is shown that it is not possible to be certain of the fundamental frequency of oscillations in which harmonics are present by observing only the frequency of a heterodyne oscillator which gives zero pitch of a combination tone.

Two methods are then given for obtaining the fundamental with certainty, the first depending on the measurement of the "width" of a combination tone, and the second on picking out the harmonics of the unknown circuit one by one by means of a resonance circuit.

In conclusion, I should like to thank Sir J. J. Thomson for suggesting this work and for the kind help he has given me during its progress.

8 Emerson Road, Harborne,
Birmingham,
June 15, 1925.

---

CVII. *Predicted Ionization-Potentials of Niton and Hydrofluoric Acid. By* George Glockler, *Ph.D., National Research Fellow in Chemistry, U.S.A., California Institute of Technology, Pasadena, California*.*

TURNER† predicts on the basis of an empirical rule connecting the quantum-defect with atomic number the ionization-potential of niton to be $27{\cdot}5 \pm 1{\cdot}5$ volts, and that of hydrogen fluoride to be $17{\cdot}9 \mp 0{\cdot}5$ volts.

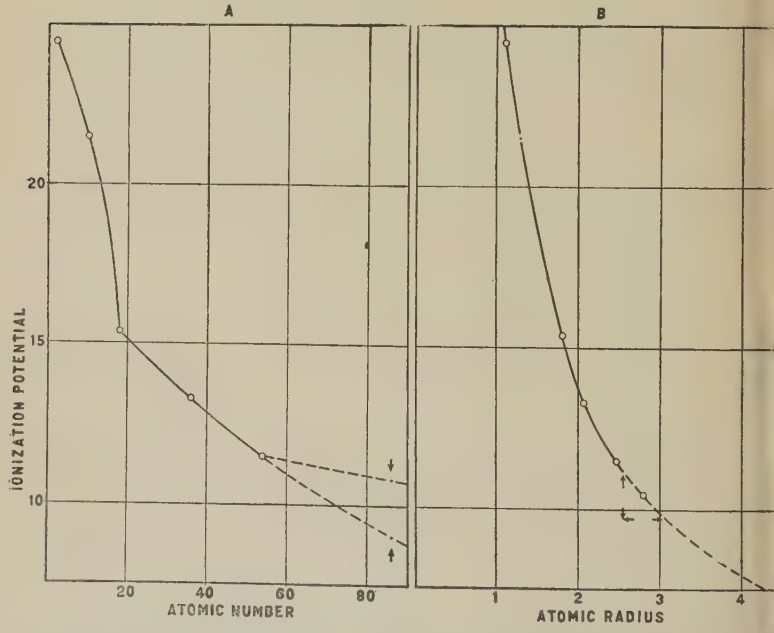
Since the ionization-potentials of niton and hydrofluoric acid will be difficult to determine experimentally, estimated values for them are of importance. For this reason I would like to point out that the above values do not agree with predictions made on the following basis :—

*Niton.*—The first method used rests on the assumption

* Communicated by the Author.
† Phil. Mag. xlviii. p. 1010 (1924).

that the relation between ionization-potential and atomic number found for the first five rare gases holds for all six of them. Throughout the periodic system it is found that within a sub-group the ionization-potential decreases with increase of atomic number. The only exception known to date exists in sub-group II, Zn–Cd–Hg. Mercury has a higher ionization-potential than either zinc or cadmium. Disregarding this exception the ionization-potentials of the rare gases as given by Hertz * were plotted against their atomic number as shown in fig. 1 (A). By simple extrapolation the ionization-potential of niton is found to be 9 volts.

Fig. 1.




It might be said that the straight extrapolation A–Kr–Xe–to Nt is not permissible, since a break occurs in the curve at argon, where now shells of 18 electrons are being added in the process of atom building, instead of shells of 8 electrons as is the case between helium and argon. If the supposition is made that the curve should show the same change in slope at xenon as at argon, then the extrapolation gives 11 volts for the ionization-potential of

* *Naturwissenschaften* No. 52, p. 1211 (1924).

niton. It should be noted that the ionization-potentials of the heavier elements of a group are always of nearly the same magnitude, so that a value of 10 volts fits this general rule, while Turner's value of 27 volts does not.

The second method used is the application of Eve's * rule to the rare gases. This rule states that the product of ionization-potential and atomic radius is a constant within a sub-group. The question arises as to which atomic radius to use. However, the results are the same whether kinetic theory †, or Bragg ‡, or Born § radii are used. The predicted ionization-potential is in the neighbourhood of 10 volts. In order to apply this rule the atomic radius of niton must be known. I have calculated it from the diffusion-coefficient ‖ of the gas in air. Using the values ·08 determined by Rutherford and Brooks ¶ and 0·100 (1 atmosphere, 10° C.) found by Curie and Danne **, the radius of niton is found to be $2{\cdot}80 \pm {\cdot}25$ ångströms. Extrapolating the radii of the other rare gases when plotted against atomic number, gives a value for the niton radius of 2·60 to 3·00 ångströms. The kinetic theory radii of the rare gases taken from Jeans †† and their ionization-potentials are given in Table I. and fig. 1 (B).

TABLE I.

| Gas. | Atomic Number. | Ionization-potentials. | Kinetic theory radius in ångströms. | Constant of Eve's rule. |
|---|---|---|---|---|
| He ..... | 2 | 24·5 exp. | 1·10 exp. | 27·0 |
| Ne ..... | 10 | 21·5 „ | (1·29) (interp.) | (27·7) |
| A ..... | 18 | 15·4 „ | 1·82 exp. | 28·0 |
| Kr ..... | 36 | 13·3 „ | 2·07 „ | 27·6 |
| Xe ..... | 54 | 11·5 „ | 2·44 „ | 28·0 |
| Nt ..... | 86 | $(10{\cdot}0 \pm {\cdot}9)$ calc. | $2{\cdot}80 \pm {\cdot}25$ exp. | (27·7) |

* Nature, June 30, 1921.
† Jeans, 'Dyn. Theory of Gases' (1921), p. 327.
‡ Phil. Mag. xl. p. 169 (1920).
§ *Zt. f. Phys.* i. p. 48 (1920).
‖ Jeans, *loc. cit.* pp. 316 & 323.
¶ Chem. News, April 1902.
** *Comptes Rendus*, cxxxvi. p. 1314 (1903).
†† The kinetic theory radii given by Jeans differ from the ones obtained by Chapman (Phil. Trans. Roy. Soc., A, ccxvi. p. 279 (1916)) and Rankine (Proc. Roy. Soc. xcviii. p. 360 (1920)). These latter ones are smaller. However, the ionization-potential of niton again is found to be 10 volts.

From the last column it is seen that Eve's rule applies to the rare-gas group, and the ionization-potential of niton is predicted to be 10 volts.

*Hydrogen fluoride.*—From grating energies Grimm and Herzfeld* calculate the difference between the heat of dissociation of molecular fluorine and the electron affinity of atomic fluorine to be $33 \pm 15$ large cal. This value may be used in the following thermochemical consideration to calculate the ionization-potential of hydrogen fluoride.

TABLE II.

| | | |
|---|---|---|
| (1) Dissociation ..... | $\frac{1}{2}H_2 \rightarrow H$. | $\frac{1}{2}D_{H_2}$ = 2·00 volts. |
| (2) ,, | $\frac{1}{2}F_2 \rightarrow F$. | $\frac{1}{2}D_{F_2} - E$ = −1·52±·7 volts. |
| (3) Electron affinity . | $E^- + F \rightarrow F^-$. | |
| (4) Ionization .. ..... | $H \rightarrow H^+ + E^-$. | $I_H$ = 13·52 volts. |
| (5) Heat of formation | $HF\ (gas) \rightarrow \frac{1}{2}H_2 + \frac{1}{2}F_2$. | Q = 1·67 volts. |
| (6) Ionization ..... | $H^+ + F^- \rightarrow HF\ (gas)$. | $I_{HF}$ = 15·67±·7 volts. |

The highest experimental value for the heat of dissociation of hydrogen known to me is the one determined by K. Wohl †. It has been taken so as not to favour a low value for the ionization-potential of hydrogen fluoride. The only uncertain value in the above calculation is the sum of steps (2) and (3). This difference would have to be positive, *i. e.* $D > E$ to make the ionization-potential 17·9 volts. For all the other halogens this difference is negative, *i. e.*, $E > D$.

The above value of $15{\cdot}67 \pm {\cdot}7$ volts can be checked independently by obtaining the heat of dissociation and electron affinity of fluorine by extrapolating the known values for the other halogens. By this method $\frac{1}{2}D_{F_2}$ is found to be 1·4 volts and $E_F = 3{\cdot}7$ volts, so that the difference is −2·3 volts. Using this independent value in the above thermochemical calculation, the ionization-potential of hydrogen fluoride is found to be 15·0 volts.

*Summary.*

1. The kinetic-theory radius of niton has been calculated from the diffusion coefficient of the gas in air to be $2{\cdot}8 \pm {\cdot}25$ Å.

* *Zt. f. Phys.* xx. p. 141 (1924).
† *Zt. f. Electrochemie,* xxx. p. 36 (1924).

2. By interpolation from Eve's rule the kinetic-theory radius of neon is estimated to be 1·29 Å.

3. By methods of extrapolation the ionization-potentials of niton and hydrogen fluoride are estimated to be 10 volts and 15 volts respectively. These values differ from the ones obtained by Turner on the basis of a linear relation between quantum-defect and atomic number.

---

## CVIII. *Thermoelectric Power and the Hall Coefficient.*

*By* C. W. Heaps *.

IN 1896 it was pointed out by Beattie † that the Hall effects and the thermoelectric powers of a large number of metals have corresponding signs. Beattie also showed that the variation with temperature of these two phenomena is strikingly similar in the case of bismuth, and Wold ‡ has found the same similarity in the curves for tellurium. Trabacchi § has pointed out that the Hall effect and the thermoelectric height in tellurium-bismuth alloys vary in nearly parallel fashion as the composition of the alloy is changed. There seems to be abundant experimental evidence of a close relationship of some kind between these two phenomena, a relationship which is to be expected from the standpoint of the free electron theory of metals.

This theory gives ‖ for the coefficient of the Hall effect, $R = A/Ne$, where A is a constant, $e$ the charge on an electron, and N the concentration of free electrons in the metal. For the thermoelectric power of one metal with respect to another the theory gives $E = \frac{k}{e} \log \frac{N_1}{N_2}$, where $N_1/N_2$ is the ratio of electron concentrations in the respective metals and $k$ is a constant, usually the gas constant for one molecule.

These equations show that any factor changing the value of N for a given metal will produce corresponding changes in E and R. Temperature changes presumably change N, and the effect on E and R has been noted. It is the purpose of the present paper to show the effect on E and R of changing the strength of the magnetic field in which the specimen is placed.

* Communicated by the Author.
† Proc. Roy. Soc. Edin. xxi. p. 146 (1896).
‡ Phys. Rev. vii. p. 169 (1916).
§ *Nuov. Cim.* ix. p. 95 (1915).
‖ Richardson, 'Electron Theory of Matter,' pp. 438 and 461.

It has been known for a long time that a magnetic field alters the thermoelectric power of a number of different metals, but the explanations of the phenomenon do not seem to be very clear. E. van Everdingen * assumes that N is affected by the field ; Lownds † states that his experiment is inconsistent with the view that a magnetic field can change the thermoelectric constants of the metal. In the experiment of Lownds a bismuth-copper thermocouple was used, and it was shown that if that part of the circuit which is in the magnetic field has a zero temperature gradient then the field does not change the thermoelectric power of the couple. This result, however, by no means justifies the conclusion of Lownds that the thermoelectric constants of bismuth are unchanged by the field. It is well known that the insertion of a third metal in a thermoelectric circuit has no effect on the electromotive force, provided there is no temperature gradient in this third metal. The magnetic field, therefore, could completely alter the properties of the bismuth in the experiment of Lownds without changing the resulting electromotive force.

An experiment similar to that of Lownds was performed by Defregger ‡, but his results cannot readily be interpreted as he does not indicate whether or not the magnetic field extends completely and uniformly over his bismuth specimen. On the whole, therefore, there seems to be no vital objection to the theory that a magnetic field may change the electronic constants of a metal. Several writers § have assumed that the number of free electrons in a metal is altered by the field.

Let us suppose a thermoelectric circuit made up of two metals, one of which, like copper, is not affected thermoelectrically by a magnetic field. Let $N_1$ be the constant electron concentration in this latter metal, $N_0$ the concentration in the other metal when no magnetic field acts, and $N_H$ the concentration in a field H. Then in zero magnetic field we shall have the thermoelectric power $E_0 = \frac{k}{e} . \log \frac{N_0}{N_1}$, which in a field H becomes $E_H = \frac{k}{e} \log \frac{N_H}{N_1}$. Thus we have $E_H - E_0 = \frac{k}{e} . \log \frac{N_H}{N_0}$. Let $R_0$ be the value approached by

* *Konink. akad. Wetensch. Amsterdam, Proc.* i. p. 437 (1899). *Ann. d. Phys.* iv. p. 776 (1901).

‡ *Ann. d. Phys.* lxiii. p. 97 (1897).

§ La Rosa, *Nuov. Cim.* xviii. p. 39 (1919). La Rosa and A. Sellerio, *Compt. Rend.* clxx. p. 1447 (1920). Heaps, Phys. Rev. xii. p. 340 (1918).

the Hall coefficient as the magnetic field approaches zero, and let $R_H$ be its value in a field H. Then, since the theory as noted above makes the Hall coefficient vary inversely as the number of free electrons per unit volume in the metal, we may write $N_H/N_0 = R_0/R_H$. We thus obtain $E_H - E_0 = \frac{k}{e} . \log \frac{R_0}{R_H}$.

According to this equation, if the Hall coefficient of a metal changes as the magnetic field increases there should be a change in the thermoelectric power of the metal when it is placed in a magnetic field. It does not appear likely, however, that the equation should be capable of exact experimental verification. The free electron theory of metals upon which it is based has proved insufficient for the explanation of various thermoelectric phenomena, nor does this theory account for the positive Hall coefficient. At best, the free electron gas theory as applied to metals must be considered only as a very rough approximation to the real conditions.

Nevertheless, it was thought worth while to make an experimental test of the above relation using several different metals and determining the Hall coefficient and the thermoelectric power for the same specimen of each. These effects vary so much with different specimens that a comparison of existent data is not satisfactory. In a previous experiment* the writer has determined the Hall coefficients for specimens of bismuth and graphite. These same specimens were available for the present work. In addition, antimony and carbon specimens with side arms for the Hall electrodes were prepared and investigated.

The apparatus for measuring thermoelectromotive forces was constructed as follows. Two brass tubes, each about 20 cm. long and 0·6 cm. in diameter, were fixed parallel with each other and insulated from each other by ebonite blocks so that their centres were 1·9 cm. apart. The specimen to be investigated was then laid with its ends on the respective tubes and fixed in this position with solder. The ends of the carbon and graphite specimens were copper plated to facilitate soldering. To each brass tube was soldered a long copper wire, and these copper wires were connected through a balancing potentiometer arrangement to a moving coil galvanometer of resistance 13 ohms and having a sensitivity of about 11 mm. per microvolt. The tubes with the specimen were covered with a thick layer of cotton to insure better heat insulation, and were then placed vertically between the

* *Loc. cit.*

poles of a Weiss electromagnet. The pole-pieces were 10 cm. in diameter and 3·03 cm. apart. By rotating the electromagnet about a vertical axis the magnetic field could be directed either longitudinally or transversely with respect to the length of the specimen. Steam at 100° C. was sent through one tube, water at room temperature through the other. The resulting thermoelectromotive force was balanced by adjusting the potentiometer till the galvanometer deflexion became zero. Upon exciting the electromagnet the galvanometer was deflected, indicating a change of thermoelectromotive force of the specimen with respect to copper. Then by properly adjusting the potentiometer this deflexion could be brought to zero again and the change of e.m.f. easily calculated.

It was found that reversing the direction of the magnetic field required a somewhat changed setting of the potentiometer for balance. Such an effect is to be expected if the specimen is not of the proper uniform structure, or if it is composed of small crystals with their axes not in line with the length of the specimen. In such a case the isothermal lines in the specimen would not be parallel with the end surfaces, and a component of the transverse thermomagnetic effect would enter. As this component tends to increase the galvanometer deflexion for one direction of the magnetic field and diminish it for the other direction, its effect could be obviated by taking a mean of observations for the two directions of the field.

A series of observations was made for various magnetic fields, a bismuth spiral being used to measure field strengths. A cast bismuth rod gave about the same kind of results as were obtained with the bismuth plate. As a check on the work a short copper wire was mounted for examination in place of the bismuth. A small e.m.f. was detected here when the two tubes were at different temperatures, but it was small compared with that in the case of bismuth and graphite and was unaffected by the strongest magnetic field available.

For measuring the Hall effect in carbon and antimony the potentiometer arrangement was connected to the side arms of the specimen and a current of 4 amperes sent through the specimen, the brass tubes being used as terminals for this primary current. The Hall effect was thus measured in the usual way, by balancing the potentiometer, and the mean was obtained for two opposing directions of the magnetic field.

The experimental results are given in the following Table,

symbols being defined as above. The values of $E_0$ and $E_H$ are calculated by dividing the mean observed thermoelectromotive force by the temperature difference, $T_1 - T_2$, of the two brass tubes. The values of R for bismuth and graphite are obtained from the previous paper by the writer. A curve giving $R_H$ against H was plotted from the data of this paper, and from this curve the desired values of $R_H$ were obtained for comparison in the present work.

TABLE.

| Bismuth. $T_1=100°$. $T_2=27°$ C. $E_0=64·6$ microvolts. | | | | Graphite. $T_1=100°$. $T_2=27·5°$ C. $E°=5·96$ microvolts. | | |
|---|---|---|---|---|---|---|
| H Gauss. | $E_H-E_0$ microvolts. Transverse H. | $E_H-E_0$ microvolts. Longitudinal H. | $R_H$ (negative). | H Gauss. | $E_H-E_0$ microvolts. Transverse H. | $R_H$ (negative). |
| 900 | 0·52 | — | 14·5 | 800 | −0·14 | |
| 2500 | 1·87 | 0·85 | 10·0 | 1500 | −0·27 | |
| 3550 | 2·79 | 1·34 | 9·3 | 2500 | −0·54 | 0·60 |
| 4500 | 3·79 | 1·77 | 8·5 | 3550 | −0·87 | 0·638 |
| 5420 | 4·75 | 2·22 | 8·1 | 4500 | −1·19 | 0·675 |
| 6250 | 5·21 | 2·57 | 7·7 | 5420 | −1·54 | 0·710 |
| 6850 | 5·67 | — | 7·4 | 6250 | −1·86 | 0·742 |
| 7330 | 6·11 | 2·95 | 7·2 | 6850 | −2·11 | 0·765 |
| 7720 | 6·32 | — | 7·0 | 7320 | −2·31 | 0·783 |
| 8500 | 6·83 | 3·30 | 6·7 | 8400 | −2·72 | 0·826 |

| Antimony. $T_1=100°$. $T_2=26·5°$ C. $E_0=28·7$ microvolts. | | | Carbon. $T_1=100°$. $T_2=26°$ C. $E_0=2·2$ microvolts. | | |
|---|---|---|---|---|---|
| H. Gauss. | $E_H-E_0$ microvolts. | $R_H$ (positive). | H Gauss. | $E_H-E_0$. | $R_H$ (negative). |
| 1700 | — | 0·220 | 1700 | — | 0·43 |
| 3600 | — | 0·204 | 4400 | — | 0·41 |
| 4900 | — | 0·191 | 5500 | — | 0·40 |
| 7350 | 0·067 | 0·189 | 7150 | — | 0·41 |

In the case of carbon the apparatus was sensitive enough to detect a value of $E_H - E_0$ as small as 0·004 microvolt, but

no effect could be observed for the largest field used. It also appears probable that $R_H$ for carbon is constant within the limits of accuracy of the experiment. For bismuth it appears that an increase of thermoelectromotive force is associated with a decrease of the Hall coefficient; for graphite a decrease of thermoelectromotive force is associated with an increase of the Hall coefficient *. The equation derived above predicts such a relationship between the two phenomena.

The data for antimony are of special interest, because antimony, in contradiction with the demands of the simple theory of electric conduction, has a positive Hall coefficient. For this metal the above data show a small decrease of $R_H$ as the field increases. Only in fairly strong fields could the change of thermoelectromotive force be noted, but for these fields the change was an increase. It appears, therefore, that in spite of its anomalous position as regards the Hall coefficient, antimony behaves like bismuth and graphite as far as the relation between $R_H$ and $E_H - E_0$ is concerned.

Another point of interest in connexion with the data is that for bismuth a magnetic field parallel to the length of the specimen produces a smaller value of $E_H - E_0$ than does a transverse field. For the graphite crystal and for the carbon specimen a longitudinal field produced no measurable change of thermoelectromotive force. For antimony the direction of the field appeared to have no effect on the magnitude of $E_H - E_0$. According to the simple theory as outlined above we should not expect the direction of the magnetic field to be a factor for consideration in the case of an isotropic specimen. For a crystal, however, the magnetic properties in general vary with the direction considered, and we might expect that the number of free electrons, in addition to being a function of H, would also be a function of the direction of H. The experimental results, at any rate, may be explained in this way since the graphite and bismuth specimens were both crystalline.

It might be argued, however, that the direction of the heat current with respect to H is the important factor. To test this point the graphite crystal was mounted between the two vertical brass tubes so that the crystal cleavage planes instead of being vertical, as before, were horizontal. In this position the magnetic field could be rotated so as to be transverse or longitudinal with respect to the heat current,

* In the table the minus sign before the numbers under $E_H - E_0$ for graphite indicates that the field diminishes the electromotive force. This diminution increases as the field increases.

but with regard to the crystal the field was always parallel to the plane of cleavage. Experiment now showed that neither a transverse nor a longitudinal field affected the thermoelectromotive force to a measurable extent. This result indicates that crystal structure, not direction of heat flow, is responsible for the difference between the effects of a longitudinal and transverse field.

According to the equation $E_H - E_0 = \frac{k}{e} \log \frac{R_0}{R_H}$ we should have a linear relation between $E_H - E_0$ and $\log R_H$. In the

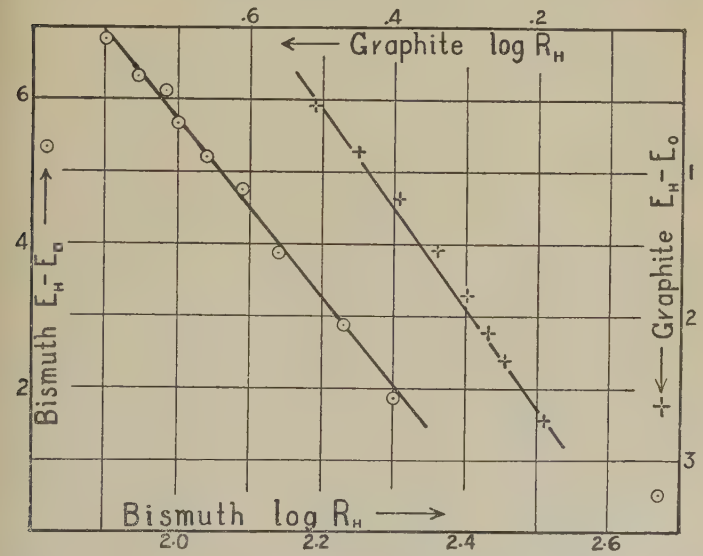



diagram these quantities are plotted against each other. The straight line drawn through the points (circles) for bismuth appears to represent the data in a satisfactory way, except for one observation made in a small magnetic field where chances of error are great. This one large departure seems quite obviously to be due to an experimental error.

The data (plotted as crosses) for graphite would fit a slightly curved line more accurately than the straight line drawn. It is possible, therefore, that there is some defect in the theory as applied to graphite. On the other hand, the deviation of the plotted points from the straight line may be due to some systematic error in the experiment. For example, the ends of the specimen were connected by solder to the brass tubes, and the steady temperatures of the water and the steam in these tubes were taken as the temperatures of

the graphite junctions. The temperature drop in the brass and solder was thus neglected. Now if the magnetic field alters the thermal conductivity of the graphite the temperatures of the ends of the graphite specimen may be altered by the magnetic field. This effect would not be allowed for in the method of calculation used.

Another source of error may lie in the fact that the variation of the Hall coefficient with field was measured at a temperature different from that at which the variation of thermoelectromotive force was measured. No doubt temperature would have a decided influence on the results obtained in the two cases.

The slope of the curves in fig. 1 should give the value of $k/e$. The usual theory makes $k$ equal to the gas constant per molecule. From fig. 1, however, we get values of $k$ which are from ten to eleven times smaller than this gas constant.

The metals used in the above-described experiments are the only ones, apart from the ferromagnetic metals, in which the Hall coefficient has been found to vary with the field. They are also, with the exception of the ferromagnetic metals, the only ones in which a magnetic field has been found to change the thermoelectromotive force *. It appears, therefore, that for the non-magnetic metals a Hall coefficient decreasing (or increasing) with strong fields is an indication that the field will increase (or decrease) the thermoelectromotive force of the metal. From the published data on the ferromagnetic metals it is hard to draw conclusions because of the difference in results obtained with different specimens. For iron the Hall coefficient appears to diminish as sufficiently strong fields are secured †, and numerous observers have found the thermoelectromotive force of iron with respect to copper to be increased by a magnetic field. In some cases a saturation effect is secured as the field increases; in others the effect becomes smaller, or even negative, for strong fields.

Cobalt and nickel behave like iron as regards the Hall coefficient. Their thermoelectromotive forces, however, have been found to be diminished by a magnetic field, though Bidwell ‡ reports the thermoelectromotive force of his iron

* Lloyd (Am. Journ. Sci. xii. p. 57, 1901) it is true, has observed a closely related phenomenon, the thermomagnetic longitudinal potential difference, in tellurium.

† L. L. Campbell ('Galvanomagnetic and Thermomagnetic Effects,' p. 42) saysthat the coeffiicient increases, but this statement seems to be an error.

‡ Proc. Roy. Soc. Lond. lxxiii. p. 413 (1904).

and nickel specimens to be affected in the same way by the field.

Zahn and Schmidt * have found that the Hall coefficient of Heusler alloy decreases as the field increases ; Grondahl and Karrer † in several specimens found a magnetic field to increase the thermoelectromotive force.

It seems probable that the phenomena of ferromagnetism introduce complications which are not contemplated in the simple theory given above. This theory, however, may be considered as at least a step in the right direction when applied to non-ferromagnetic substances.

The Rice Institute,
Houston, Texas.
April 17, 1925.

---

## CIX. *Magnetic Quality in Crystals.* *By* J. Forrest, *M.A., B.Sc., University College, Dundee* ‡.

THE following note gives in brief outline a synopsis of a research the object of which is to carry the theory of molecular magnetism in solids a stage further than its present position,—in effect (i.) to discriminate magnetic lattices in crystals and compare these magnetic arrangements with the structures found by X-ray methods, and (ii.) to investigate the stability of various arrangements of magnetic doublets.

The full theoretical analysis and experimental details and results will shortly be given elsewhere (Proc. R.S. Edin.).

### (I.) *Discrimination of Magnetic Lattices.*

In modern books on Physical Crystallography (*v.* Tutton, Groth, &c.) we find the results of Faraday, Tyndall, and Plucker quoted to indicate the magnetic quality of crystals. These workers suspended crystalline spheres in uniform fields by various axes, and by the deportment of the substance in the field discriminated qualitatively the principal directions of induction therein, thus finding in general a maximum, a minimum, and an intermediate principal value, each of which was identified with the appropriate crystalline spacing. All these workers classed crystals belonging to the cubic system as magnetically isotropic. After the

* *Verh. D. Phys. Ges.* ix. p. 98 (1907).
† Phys. Rev. xxxiii. p. 531 (1911).
‡ Communicated by the Author.

theories and ideas of Poisson, Weber, Ampère, Maxwell, and Ewing had laid the foundations of the molecular theory of magnetism in solids, the next development of the subject came in the experimental researches of Weiss and Quittner, who dealt with the cubic crystal magnetite and showed conclusively that it was not magnetically isotropic. Weiss also worked with the rhombohedral crystal pyrrhotine in which he found a "magnetic plane," perpendicular to which the crystal could not be so readily magnetized, and also showed that the magnetic quality of the crystal does not represent hexagonal symmetry.

Professor W. Peddie * was led by these results of Weiss † and Quittner ‡ to work out a discussion of magnetic quality in homogeneous arrangements of molecular magnets. He dealt with two cases of cubic arrangement and also gave an outline of a general treatment by which any arrangement could be dealt with. In two of these papers he indicates how such a theoretical discussion explains with great exactness the magnetic quality of magnetite and pyrrhotine. In the first part of my research I have worked out this theory in detail and applied it more definitely to the problem of discrimination of magnetic lattices in specific crystals, all of which were much more weakly magnetic than magnetite or pyrrhotine. For the purposes of the second part of this investigation, I have rebuilt the theory *ab initio* from the point of view of the magnetic Potential Energy in a homogeneous assemblage of equal magnetic doublets.

The fundamental fact, on which this method of magnetic lattice discrimination is based, is that when a crystalline portion of matter has a magnetic field applied to it, it is magnetized, not necessarily in general in the direction of the field as would be the case if the substance were purely isotropic, but in general in some direction inclined to that of the external field. The intensity of this magnetization, developed obliquely to the external field, can be replaced effectively by two components, one parallel to the external field and another perpendicular to that direction. On the experimental side of the work these components of magnetization are measured for varying orientation of (high) magnetizing fields in circular plates cut in chosen planes from selected crystals. The parallel component with its variations was measured by a "drag" method, the movement

* W. Peddie, Proc. R. S. Ed., 1905, p. 1025 ; 1908, p. 644 ; 1912, p. 216.

† P. Weiss, *Journal de Physique*, 1896, and iv. (1905).

‡ V. Quittner, *Ann. d. Physik*, xxx. (1909).

of the specimen plate in a non-uniform field being controlled by the bending at the mid-point of a long copper wire under tension. The measurement of the transverse component was effected by rotation of the specimen in stationary uniform fields and also by rotation of uniform fields in azimuth about a stationary specimen.

In the derivation of theoretical estimates of these components the Potential Energy of two parallel similar magnetic doublets is found, the potential between any two poles being assumed to be inversely proportional to their distance apart, as the simplest law. The expression for this mutual Potential Energy is expanded as a series of Zonal Harmonic terms, and general expressions for the components of force at a pole of one of the pair, parallel and transverse to their direction, are deduced by appropriate differentiation. These latter results are then extended by a process of summation to give similar components of the internal force in any regularly arranged three-dimensioned system of co-directed similar magnetic doublets. The final expressions for these parallel and transverse components agree, (as they must), with those found by Prof. Peddie in his papers where he deals directly with the internal force. Each term of these Zonal Harmonic series giving the two components is one degree higher in $(a^2/\rho^2)$ than the preceding term, where '$a$' is the semi-length of a magnetic doublet and '$\rho$' is the distance apart of nearest neighbours in the whole set of doublets. The strongest existent term is dealt with on the assumption that the value of $(a^2/\rho^2)$ makes the next term negligible compared with that dealt with. The terms in the series are functions of the direction cosines of the internal force, of coefficients which involve summations of functions of the coordinates of the centres of the magnets, and also of the spacings of the arrangement. These spacings are equal to or proportional to the crystal spacings. Hence these coefficients can be found for any regular arrangement of centres by arithmetical evaluation and summation throughout the medium about an origin therein. In every case each such constant is the sum of a convergent numerical series and its value necessarily differs for different lattice arrangements of the centres.

The theoretical expressions for the parallel and transverse components of force can be made applicable to any desired plane of the various crystallographic systems by geometrical and other reasoning. It has been found convenient to deal with the co-ordinate, *i. e.* (1, 0, 0), planes and in extreme cases also with the (1, 1, 1) planes. Hence we can deduce

the nature of the variation of these components in any plane of a crystal for any lattice arrangement of the centres of the doublets, as the co-directed system of doublets takes all possible orientations in that plane. As it is the variation of the internal force that causes the variation of the magnetization, the nature of these variations must be practically the same for force and magnetization. From this variation we can find positions of maximum and minimum induction in any plane of a crystal of known geometry for any lattice arrangement of centres. By comparison of the experimentally obtained variations of these components of magnetization for varying orientation of the external field in any chosen plane of the crystal with the theoretical variations of internal field appropriate to the various possible lattices, we can discriminate the lattice arrangement of the centres of the doublets, *i.e.*, the magnetic lattice. In the meantime the problem is limited to one of discrimination of positions of maxima and minima.

The experimental curves of variation of the parallel component in (1, 0, 0) planes of crystals belonging to the ortho-rhombic system consist of indented ovals with positions of maxima and minima separated by 90°. In the cubic system equal minima occur in these planes 90° apart, with intermediate equal maxima. In the (1, 1, 1) planes of the cubic and trigonal systems hexagonal symmetry is shown by the occurrence of maxima and minima at intervals of 30° or 60°. The curves of variation of the transverse component, which is measured by a couple, consist of loops, successively of opposite signs, with zero values coinciding in position with maximum and minimum values of the parallel component in the same plane. Turning values of these components coincide with crystallographic axes except in crystals belonging to the oblique systems.

In some cases the magnetic lattice is found to be of the same nature as the molecular or main atomic lattice discriminated by X-ray methods. In other cases it would appear to be otherwise. It is to be noted that for each crystal dealt with the standard point-arrangements possible for the equivalent magnets in the corresponding crystallographic system were all tested for agreement. In testing the theory I dealt with about twenty different crystalline substances, including examples from all the different crystallographic systems.

In many cases the solution, for the correct magnetic lattice to fit the structure, is unique, only one of the standard point-systems fitting such cases. In other instances more

than one lattice gives the actual relative positions of maxima and minima. In all cases there is found in the experimentally determined parallel component a constant effect not given by the simplest form of the theory, and in the experimentally determined transverse component curves of magnetization there is found, on approach to the axes of minimum force, a flattening effect. This latter effect enables us to distinguish these directions of minimum force in any plane of the crystal by means of the transverse component. In the *Cubic System* the crystals dealt with were (1) the Cubic Alums, (2) Iron Pyrites, Cobaltite, Copper, Sodium Chloride, and Fluor-spar. The main atomic and molecular lattices of these are the Face-Centred Cube System according to X-ray results. (1) In the cube-face planes (*i. e.*, 1, 0, 0) the Cubic Alums, like Magnetite and crystals of Iron, are found to have magnetization minima along the cube edges (*i. e.*, quaternary axes) and maxima along the Cube-face Diagonals (*i. e.*, Binary Axes). The theory predicts that this will be the case for the Face-Centred Cubic Magnetic Lattice or for the Body-Centred Cubic Magnetic Lattice. According to X-ray workers (Bragg and others) the main atomic lattice of Magnetite is the Face-Centred Cubic System and the atomic lattice of Iron is the Body-Centred System. Vegard has shown that the main atomic lattice of the Cubic Alums is the Face-Centred Cubic System. Hence in the cases of Magnetite, Iron Crystals, and the Cubic Alums there is distinct agreement between the magnetic lattice and the main atomic lattice found by means of X-rays.

(2) The rest of the above cubic series (*i. e.*, $FeS_2$, CoAsS, Cu, NaCl, and $CaF_2$) have magnetization maxima along the Quaternary Axes (*i. e.*, cube edges) and minima along the Binary Axes (*i. e.*, Cube-Face Diagonals), as is demanded by the theory for the Simple Cubic Magnetic Lattice. Hence in these cases, in which the main X-ray atomic lattice is the Face-Centred System, the magnetic and atomic lattices are not the same, unless maxima and minima are interchanged. The alternative of interchange of positions of maxima and minima in any plane of the crystal will be discussed later.

*Ortho-rhombic System.*—In the cases of Potassium Sulphate and Ammonium Sulphate more than one magnetic lattice gives the relative intensities, but it is notable that the basic atomic lattice found by X-rays by Ogg and Hopwood and discussed by Tutton, best explains the behaviour of the crystal in the field. For Nickel Sulphate ($7H_2O$) the Diagonal Prism Magnetic Lattice alone fits, and in the cases of Potassium Ferrocyanide and Potassium Ferricyanide

the Simple Prism Magnetic Lattice alone is suitable. In all these cases, all the possible standard point-systems were tested as magnetic lattices. In some of these cases, agreement is obtained by interchanging experimentally found positions of maxima and minima, *but it is notable that in any case where this is done the lattice selected gives striking agreement with the relative intensities and with the behaviour of the crystal in the field.*

*Tetragonal System.*—Nickel Sulphate ($6H_2O$) :—Of the standard point-systems possible in this case, the Diagonal Tetragonal Prism (Magnetic) lattice alone fits.

*Trigonal System.*—Calcite :—Here the Face-Centred Rhomb point-system alone fits, and as this is the main atomic lattice found by X-ray methods, there is correspondence here.

Quartz :—The original molecular lattice proposed by Bragg and also his latest proposed atomic lattice (modelled on Barlow's spiral structure), were both tested, and agreement was found with the latter but not with the former, *i.e.*, the spiral main atomic lattice gives a satisfactory magnetic lattice. Bismuth and Antimony :—For these substances, the standard trigonal lattices were again all tested, and also the latest atomic lattice proposed by James and Tunstall, but definite agreement is found with none of these.

*Tri-clinic System.*—Copper Sulphate ($7H_2O$), Manganese Sulphate ($7H_2O$) and Potassium Dichromate were dealt with. In this system there is only one point arrangement to be tested, viz., the Simple Tri-clinic Prism, and in these crystals close agreement is found for that Magnetic Lattice as regards positions of maxima and minima, but only by interchange of positions of maxima and minima in some planes though not in others. In some sections direct agreement is found. Whether this reversal in some planes only is necessary for agreement in all crystals belonging to the oblique system is so far uncertain.

*Mono-clinic System.*—The Mono-clinic Alums (*e.g.* Nickel Ammonium Sulphate) were tested, and in these cases either the Simple Mono-clinic Prism Magnetic Lattice or the Diagonal Prism Lattice suit. Chlorate of Potash, a knowledge of the magnetic lattice of which in required in Part II. of this research, was also investigated and the Diagonal Monoclinic Prism Magnetic Lattice alone fits. In this case interchange of maxima and minima is necessary, but the solution obtained is unique and gives striking agreement with the behaviour of the crystal in the field.

*Conclusions.*—The interchange of positions of maxima and

minima necessary in some cases to give a satisfactory magnetic lattice, and the constant effect found in the parallel component in all cases, are not accounted for by the simplest application of the theory. There is a possibility that this latter effect may be due to thermal motions which have been ignored in the derivation of the theory. Again, part of the constant effect may, in the light of the Bohr-Rutherford atom structure, be due to the nucleus, or since there may be difficulties in the idea of a magnetic nucleus it might be ascribed to the more central electron orbits. As regards the interchange of positions of maxima and minima, it is to be noted that the unit magnetic cell, containing the single equivalent magnet presumed to be capable of representing the resultant effect, contains actually in general a group of atoms or molecules, some of which may be paramagnetic while others are diamagnetic. Hence, as the laws of paramagnetic and diamagnetic induction are different, it is necessary to recognize an *à priori* possibility that the internal field should be represented as the sum of a paramagnetic part and a diamagnetic part, which vary differently in like directions. Prof. Peddie has suggested to me that herein may be contained a possible explanation of interchange of maxima and minima. This interchange, necessary in many cases to give a solution (and that a perfectly fitting one), and especially the partial interchange found in the Tri-clinic System, appears to dispose conclusively of any idea that the magnetic lattice found will in all cases correspond with the "Lattice-form" or cell-arrangement. In fact a survey of the experimental results conveys the impression that in many cases there is distinct evidence of the super-position of the magnetic effects of differently acting groups of atoms.

The individual results indicate primarily that: (*a*) the variation of the magnetic quality of a crystal depends (1) on its structural geometry, *i. e.*, spacings and axial angles and (2) on its magnetic lattice; and (*b*) that cubic crystals are not magnetically isotropic but their magnetic quality is represented by the quartic surface, derived from the theory by Professor Peddie in his first paper on the subject, and further elaborated and discussed from the point of view of Potential in this research.

## (II.) *Stability of Magnetic Lattices.*

This part of the research consists of a discussion of the stability of regular arrangements of magnetic doublets from the point of view of their magnetic interactions, in particular

under an applied field strong enough to produce co-direction of the system, *i. e.*, saturation. The magnetic energy alone is considered and thermal effects are meantime ignored.

A general expression in Zonal Harmonics is derived for the mutual Potential Energy of two equal magnetic doublets the axes of which contain any angle. Special cases are dealt with in which that angle is (1) 0°, (2) 180°, and (3) 90°. These three cases are extended to include any regularly arranged system of equal doublets. Here the expression for the Potential Energy is of the same type as for the force and the strongest term has again to be dealt with. In some cases several terms are dealt with. In any given choice of possibilities in mode of growth, the most probable of occurrence, other things being equal, will be that which corresponds to greatest exhaustion of Potential Energy. The Potential Energy of such a system, when co-directed, changes with its orientation with reference to the coordinate axes, *i. e.*, as the orientation changes within the geometrical arrangement of the individual centres. Exhaustion of all such possible orientations gives the minimum Potential Energy possible, and so the arrangement capable of the greatest stability is indicated. Once more the coefficients in the expression for the Potential have to be evaluated arithmetically by triple summation throughout a definite sphere of influence in the medium.

The same process is applied to give the Potential Energy of any regular non-codirected arrangement of similar elements the axes of no two pairs of which contain the same angle. The potentials of individual doublets are found in the field of the member at a chosen origin and by addition of potentials the whole internal potential energy is found.

Dealing with co-directed systems a discussion is given of the *Stability of the Cubic Magnetic Lattices*, and the Face-Centred System is found to have the maximum possible stability. Next follow in order of descending stability the Simple Cube and the Body-Centred Cube Systems. The Diamond Cubic Lattice is shown to be a more stable form of the Face-Centred System. In addition the Face-Centred and Body-Centred Systems contain more directions of stable orientation than unstable ones. The Simple Cube Magnetic Lattice contains more unstable directions than stable ones

*The non-Magnetic condition* in the cubic system is discussed with special application to non-magnetic Iron. The magnetic lattice of an iron crystal is taken to be the Body-Centred System in accordance with the results in Part (I.)

of this investigation. Three particular non-magnetic arrangements are depicted, with alternate layers oppositely co-directed or containing doublets variously oriented in closed chains, and these are found to have greater possible stability than the corresponding co-oriented system. On this point of view the magneton may be a property of the structure rather than of the molecule or atoms. Similarly multiple values for atomic or molecular susceptibility may be explained apart from any question of the existence of the magneton. *Barlow's Closest Packed System* and the Face-Centred Cubic System are compared as possible magnetic lattices and the latter is found to have greater possible stability than the former.

*Conditions for Twinning* in the Face-Centred Cubic System are discussed in the same way, following Kelvin's idea of the formation of a twin by the filling up of alternative sets of hollows *. By piling up layers of magnetic members in this way on the octahedral plane alternatives are found which can have greater possible stability than the normal Face-Centred Cubic System. A similar investigation can be given of growth on both sides of the initial twin plane. In this system a twinned growth is found, which has exactly the same stability as a normal untwinned growth. Formation of a twin is shown to depend also on the actual value of the ratio $(a/\rho)$, where '$a$' is the semi-length of a magnetic doublet and '$\rho$' is the distance apart of nearest neighbours.

Finally, the occurrence of twinning in the monoclinic crystals of Chlorate of Potash is discussed in the same way, *i. e.*, growth from alternative sets of hollows giving a more stable arrangement. The Magnetic Lattice is found to be the Diagonal Monoclinic Prism one, which is also shown to have, layer by layer, greater stability than the other possible arrangement in this system, viz., the Simple Monoclinic Prism.

So far as the arithmetical summations for the constants have been effected, there is, from the point of view of magnetic stability, no direct evidence of the possibility of occurrence of twinning within a thickness of five layers, and further work will be necessary to settle the question definitely.

The majority of the results in both parts of this research appear to justify the initial fundamental assumption as to the small size of $(a/\rho)$ and to prove the existence of the magnetic lattice, *i. e.* the simple homogeneous system of

* Kelvin: Baltimore Lectures.

crystallinely arranged magnetic bipoles, which is magnetically equivalent to the actual atomic arrangement in its non-isotropic nature.

Future work will deal with atoms of all types in the hope of obtaining a more complete solution in some of the above cases. Such analysis, taking account of atoms of all kinds, may explain the interchange of maxima and minima mentioned above, and also account for the diamagnetic quality of crystals the component atoms of which are paramagnetic and the weak susceptibility of many crystals in which one constituent kind of atom is strongly magnetic.

---

CX. *The Allotropy of Manganese.* *By* A. J. Bradley, *M.Sc., Ph.D., The Physical Laboratories, University of Manchester* *.

[Plate XXXIII.]

## 1. *Introduction.*

MANGANESE is the only common metal whose crystal structure has never been ascertained. Photographs of the X-ray powder spectrum have been taken by several workers, notably by J. F. T. Young †. The lines observed on Young's film do not form a simple pattern such as would be given by a cubic, hexagonal, trigonal, or tetragonal structure. This fact is easily ascertained by the use of Hull and Davey's graphical method of crystal analysis ‡.

This is very remarkable, since all other metals with the exception of mercury have quite simple structures, and it suggests that the metal may possess other abnormal qualities. The peculiar magnetic behaviour of the Heusler alloys, which contain large proportions of maganese, may be a case in point. Young found that these substances are mixtures of body-centered and face-centred cubic lattices, and that in general they were much more ferromagnetic when they contained large proportions of the body-centered variety. It had been suggested that the ferromagnetism of the alloys was due to the presence of an allotropic form of manganese, but Young pointed out that elementary manganese no longer existed in the alloy, since the lattices were both quite homogeneous.

* Communicated by Prof. W. L. Bragg, M.A., F.R.S.

† J. F. T. Young, Phil. Mag. xlvi. p. 291 (1923).

‡ A. W. Hull and W. P. Davey, Phys. Rev. xvii. p. 549 (1921).

On the other hand, it seems reasonable to believe that the internal state of the manganese atom will not be the same in the two forms of the alloy, and that this difference may be reflected in a different behaviour of the pure metal under different conditions. It would, therefore, not be surprising to find that the element was allotropic, and an investigation of its crystal structure appeared to be of great interest from this standpoint.

## 2. *Experimental.*

The crystal structure of manganese was first investigated by the method of the X-ray powder photograph. The apparatus has been somewhat modified from that described by the author in a previous paper *. As before, a hot tungsten filament was used for cathode, but an iron anticathode took the place of the original copper target, this change being necessitated by the enormous absorption of copper radiation by manganese. An iron anticathode is particularly useful, since manganese absorbs K$\beta$ iron radiation very strongly, reflecting only the $\alpha$-rays of wavelength 1·932 Å. Two cameras were employed so that two photographs could be taken simultaneously by radiation from opposite sides of the anticathode. The cameras were of different sizes, their diameters being 1 inch and 1·5 inches respectively.

The specimens of manganese to be examined were ground down in an agate mortar until the particles were so fine as to show almost no crystalline lustre when observed by the naked eye. This operation occupied over half-an-hour in many cases. The powdered metal was made into a paste with canada-balsam thinned down with toluene and mounted on a hair, to which it readily adheres to form a thin cylinder of any desired thickness; 0·2 to 0·4 mm. is about the optimum size. This hair was mounted vertically at the centre of the camera, and the latter adjusted so that the path of the X-rays from the anticathode to the powder made an angle of about 4° with the surface of the anticathode. In this way, the surface of the anticathode subtended at the centre of the camera, and the powder cylinder, are equivalent to two vertical slits producing a parallel beam of rays, and no other slits are required except to screen the more divergent portion of the beam from the film. Small lead

* Phil. Mag. xlvii. p. 657 (1924).

stops are, however, required to cut down the height of the beam, which is very important if sharp lines are required. The exposure under these circumstances was about 8 milliampere-hours, the voltage being 25,000 to 27,000.

### 3. *The Isolation of the Allotropes.*

Many samples of manganese from quite different sources and of varying degrees of purity were examined by the powder method, and a somewhat surprising result was obtained. No two samples gave quite the same type of photograph, and none gave a pattern identical with that obtained by Young, a reproduction of which is given in this paper. At first sight, one might suppose this peculiar behaviour to be due to the presence of varying amounts of different impurities. This, however, is not a likely explanation, for it is well known that the addition of quite large amounts of foreign ingredients does not usually change the type of structure of an element, but only causes a slight change in the lattice spacings. It will be shown later that the composition of the specimen has very little effect on the structure assumed by the manganese.

A clue to the true explanation of the phenomenon is given by a more careful inspection of the various photographs. It then becomes clear that only three distinct series of lines run through the whole set. One of these patterns occurs only on the film obtained from electrolytic manganese, and will be referred to in greater detail later. The other two series of lines occur on every specimen of commercial manganese from whatever source obtained and whatever the degree of purity of the sample or its method of manufacture. It is clear that in this case we are dealing with mixtures of at least two allotropic modifications, which are present in different proportions in every sample. The first step in the solution of the problem was therefore to isolate each allotrope in turn. For this purpose heat treatment was tried.

A method of tackling the problem is suggested by a consideration of the behaviour of iron. Westgren and Phragmén* have shown that precisely the same X-ray photograph is obtained from a quenched specimen as from one which is heated to 1100° during the time of exposure to the radiation. On the other hand, a specimen heated to 1425° during exposure gives a pattern of lines typical of

* A. Westgren and G. Phragmén, Iron and Steel Inst. Journ. cv. p. 241 (1922); cix. p. 159 (1924).

a pure body-centred structure, whereas one quenched from the same temperature shows signs of considerable change to the face-centered form during cooling. In the case of manganese the brittle nature of the element makes it difficult to obtain in the form of wire, so that it is much more difficult to heat during exposure to X-rays. For this reason quenched specimens were examined. Probably no change occurred on quenching, since only temperatures up to 1105° were used, and specimens heated to 1105° and 900° gave identical results. The manganese in the form of solid pieces was introduced into a silica tube 30 inches long and one inch in diameter, and the latter was then closed at each end by means of a rubber bung. One end was connected by glass tubing to a Gaede vacuum-pump and pressure-gauge so that the tube could be evacuated during the heating of the specimen.

The silica tube was surrounded about its centre by a nichrome-wound furnace about one foot in length, the temperature being maintained by means of current taken from the supply main at 200 volts and passed through suitable resistances. The whole apparatus took some considerable time to attain a constant temperature, and was therefore usually heated for about 24 hours with the current as constant as possible The vacuum did not remain perfect during this period, a leak equal to about 1 cm. of mercury occurring owing to the porosity of the silica tube and to the use of rubber connexions. The temperature was measured by means of a platinum-iridium couple inserted between the evacuated tube and the inner wall of the furnace. This was used in conjunction with a millivoltmeter.

At first quite low temperatures were tried, but afterwards the temperature was raised by stages of about 100° to 1105°. In each experiment, after heating for about 24 hours, air was admitted to the tube, and the specimen was quickly knocked out by means of a long rod into a jar of cold water, being thus cooled from the temperature of the furnace to room temperature in a second or two. A portion of each quenched specimen was ground down and a powder photograph obtained in the usual manner. The results of these tests are summarized in Table I. The three patterns of lines are indicated by the symbols $\alpha$, $\beta$, $\gamma$, and apparently correspond to all three allotropes*. Eight distinct specimens, referred to as A, B, C, D, E, F, G, H, were examined, and it will be seen that only G definitely

* Reproductions of films showing $\beta$ and $\gamma$ lines are given on Pl. XXXIII.

gave the $\alpha$ pattern. The specimens G and H were obtained electrolytically, and will be considered in greater detail later. The first row of the table shows the result of an examination of the specimens before heat treatment. The specimen A, which was the purest obtainable commercially, gave only the $\beta$ lines, as did the specimen B, obtained by sublimation on to

TABLE I.

| Temp. of heating. | A. | B. | C. | D. | E. | F. | G. | H. |
|---|---|---|---|---|---|---|---|---|
| Untreated. | $\beta$ | $\beta$ | trace $\gamma+\beta$ | trace $\gamma+\beta$ | some $\beta+\gamma$ | some $\beta+\gamma$ | $\alpha$ | $\alpha$ (?) |
| 120°..... | ... | ... | ... | ... | ... | ... | ... | $\alpha$ (?) |
| 150°..... | ... | ... | ... | ... | ... | ... | ... | $\beta$ |
| 300°..... | $\beta$ | ... | trace $\gamma+\beta$ | ... | some $\beta+\gamma$ | ... | $\beta$+oxide (?) | |
| 400°..... | $\beta$ | ... | $\beta$ | ... | some $\beta+\gamma$ | ... | $\beta$+oxide (?) | |
| 500°..... | $\beta$ | ... | ... | ... | some $\beta+\gamma$ | | | |
| 600°..... | $\beta$ | ... | $\beta$ | ... | some $\beta+\gamma$ | | | |
| 670°..... | some $\beta+\gamma$ | ... | some $\beta+\gamma$ | ... | some $\beta+\gamma$ | | | |
| 750° ..... | $\beta+\gamma$ | ... | $\beta+\gamma$ | ... | $\beta+\gamma$ | | | |
| 820°..... | some $\gamma+\beta$ | ... | ... | ... | $\gamma$ | | | |
| 905°..... | $\gamma$ | ... | ... | ... | ... | ... | ... | $\gamma$+oxid |
| 1105°..... | ... | ... | ... | ... | $\gamma$ | | | |

a cooled portion of the tube when specimen E was heated *in vacuo* to a temperature of 1105°. It will be seen from the table that at the same time the residue of E was converted into the pure $\gamma$ modification, in which condition it remained after quenching. C and D gave almost identical photographs, as also did E and F. Consequently specimens A, C, and E were selected for heat treatment.

C was converted at 400° into the pure $\beta$ type, and further heating caused precisely the same changes as those produced

in A at the same temperature. It is therefore certain that the original difference between the specimens A and C was produced by their previous treatment. Specimen E does not behave in the same way as A and C. It was apparently impossible to convert the specimen into the pure form except by sublimation, when, of course, its composition is changed. After heating this specimen (E) to 1105°, the pure $\gamma$ specimen so obtained was submitted to further heating at 600°. Once again it reverted to its original state ($\beta$ + some $\gamma$); so it appears that no amount of heat treatment could convert this specimen completely into the $\beta$ form.

It has thus been established that manganese as ordinarily obtained in commerce exists in two modifications, and that in general any given sample of fairly pure commercial manganese is likely to contain a mixture of two allotropes in varying proportions. The state of the specimen depends chiefly on its previous heat treatment, but the presence of certain impurities (carbon?) may tend to alter the normal reaction to such treatment so that the changes do not occur at the same temperature. Any specimen when cooled quickly may apparently be kept at room temperature for an indefinite time without change of structure.

An attempt was made to determine the transition temperature at which the $\beta$ form passes into the $\gamma$ modification. On reference to Table I., it will be seen that results have been obtained for the examination of various specimens quenched from temperatures between 600° and 905°, which includes the region of transition. The specimen E appears to behave abnormally, and therefore only specimens A and C, which gave identical photographs for every temperature examined between these temperature limits, will be considered at this stage.

The table shows that, on quenching from any temperature within the region 650°–850°, mixtures of $\beta$ and $\gamma$ were obtained from specimens A and C. The higher the temperature the greater the proportion of the $\gamma$ modification. This can be explained in two alternative ways. Either we may suppose that there is a definite transition temperature, or that the structure changes gradually over a wide range of temperatures. In the first place, any transition temperature would have to be below 670°, since any specimen of $\beta$ manganese is partially converted into the $\gamma$ form after heating for some time at this temperature. If the transition temperature actually exists, the specimens which contain both $\beta$ and $\gamma$ forms must have been produced by the partial conversion of the original $\gamma$ form into the $\beta$ form during

quenching. This, however, seems most unlikely, for the time occupied during this process was usually scarcely more than one second, and in one case where the specimen was accidentally delayed in cooling no further conversion to the $\beta$ type occurred. It must also be borne in mind that the specimen C, although in the form unstable at low temperatures, was quite unaffected by heating to 300° for 24 hours, so that even at this temperature the equilibrium is entirely frozen. It seems most unlikely that a specimen cooled from 750° could, in the fraction of time between falling below 670° and becoming cooled to 300°, have changed to such an extent that 50 per cent. existed in the $\beta$ form.

We must suppose the manganese to exist in a state of isodynamic isomerism, in which the equilibrium gradually changes over as the temperature is raised. At 600° $\beta$ manganese is the stable form, but as the temperature is raised, the equilibrium shifts over to the $\gamma$ modification until at 900° $\gamma$ manganese alone is stable. The behaviour of specimen E is accounted for by supposing the addition of certain impurities to upset the equilibrium.

### 4. *Electrolytic Manganese.*

It remains to discuss the nature and behaviour of specimens G and H. These were made during an attempt to obtain pure manganese electrolytically by the method described by Allmand and Campbell *. The conditions were, as far as possible, identical with those described in their second paper. Three litres of catholyte were employed with a rotating aluminium cathode and two anodes immersed inside porous pots. In the most successful experiment the voltage was about 7, the current density being about 12 amps per square dm. The current was running for about three hours with the temperature about 25°, when the catholyte became so alkaline that hydroxide began to form. The electrolysis was then immediately suspended, and the cathode washed in dilute acid and water and dried by immersing in methylated spirits and allowing the alcohol to evaporate. The solutions which are identical with those used by Allmand and Campbell were as follows :—

Catholyte : 300 gm. $MnSO_4 . 4H_2O$
$+ 100\,gm.(NH_4)_2SO_4$/litre.

Anolyte : A saturated solution of $(NH_4)_2SO_4$.

* A. J. Allmand and A. N. Campbell, Trans. Faraday Soc. xix. p. 559 (1924) ; xx. p. 1 (1924).

The product obtained contained two distinct layers. The first deposited was soft and friable, and resembled the product obtained by grinding up the substance formed during the preliminary attempt. It was light brown in colour, in contrast with that deposited during the latter stage of the electrolysis, which was black. This black form, although readily broken into very small particles, was very resistant to further grinding in an agate mortar, and appeared to be remarkably hard. It was submitted to examination by the powder method.

The film so obtained contains very few lines, and obviously corresponds to a particularly simple structure. Only six lines stand out clearly. Two more are situated on the edge of the film, and can only just be seen. Table II. gives

Table II.

| $\frac{d}{n}$ (obs.). Å. | $\frac{d}{n}$ (calc.). Å. | Reflecting plane. | Order of intensity. | Calculated. intensity. |
|---|---|---|---|---|
| 2·134 | 2·130 | 111 | 1 | 100 |
| 1·882 | 1·882 | 200 | 3 | 39 |
| 1·778 | 1·778 | 002 | 4 | 17 |
| 1·331 | 1·331 | 220 | 4 | 19 |
| 1·296 | 1·293 | 022 | 3 | 37 |
| 1·131 | 1·128 | 311 | 2 | 56 |
| 1·082 | 1·082 | 113 | ? | 26 |
| 1·065 | 1·065 | 222 | ? | 25 |

measurements of the film. The spacings $\left(\frac{d}{n}\right)$ obviously correspond to a face-centered tetragonal lattice of axial ratio almost unity which is identical with a body-centred tetragonal lattice of axial ratio about 1·4. This can be confirmed by Hull and Davey's graphical method. The spacings fit on a graph for a body-centred tetragonal lattice of axial ratio 1·34, or a face-centred tetragonal lattice of axial ratio 0·944. The second and third lines are respectively (200) and (002), the intensity of the former being distinctly greater than that of the latter, which is therefore the basal plane. The edges of the unit cell are 3·764 Å. and 3·556 Å., the axial ratio being $= \frac{3{\cdot}556}{3{\cdot}764} = 0{\cdot}9445$.

With the spacings for (200) and (002) as standards, the spaces corresponding to a face-centred tetragonal lattice were calculated, and, as the table shows, they check up quite well with the observed values. The order of intensity of

the lines on the film agrees with the calculated values of the last column, with the exception of two lines on the edge of the film which are difficult to observe. The calculated values are obtained by dividing N, the number of co-operating planes which reflect at any particular angle, by the square of the sine of the glancing angle. This empirical rule appears to hold quite well in the present instance.

The volume of the unit cell which should contain 4 atoms is $50{\cdot}3 \times 10^{-24}$ c.c., so that each atom occupies $12{\cdot}58 \times 10^{-24}$ c.c. The weight of 1 atom is $90{\cdot}6 \times 10^{-24}$ gm., which gives a density of 7·21. The value usually given for the density of manganese varies between 6·5 and 8·0 according to the nature of the specimen examined.

The structure of manganese when obtained by electrolysis is therefore a face-centred tetragonal lattice of axial ratio 0·9445 : 1, or it may be regarded as a body-centred tetragonal lattice of axial ratio 1·34 : 1. The structure is intermediate between a face-centred cube and a body-centred cube, and represents a close packing of oblate spheroids. It is interesting to compare the distance of closest approach of atoms for manganese, iron, cobalt, and nickel. The values are 2·66 and 2·59 for manganese compared with 2·54, 2·51, 2·50 for iron, cobalt, and nickel respectively, considering the face-centred modification in each case.

It was intended to submit this specimen to heat treatment *in vacuo*, but unfortunately air obtained access and the specimen was oxidized. Further attempts were therefore made to obtain manganese electrolytically, using a bigger bulk of solution. Unfortunately all the specimens afterwards obtained were so finely divided that no real pattern of lines was obtained. In every case, however, one very strong line showed up. This corresponds to the first line on the film of the tetragonal structure. It is, however, unfortunate that the first line of each of the other two specimens ($\beta$, $\gamma$) also corresponds equally well, for the spacings are in each case about 2·1 Å., and the line is extremely broad and diffuse. It is clear that this specimen is manganese in an extremely finely-divided form, but it is impossible to say whether it is really identical with the $\alpha$ modification.

An attempt to convert it into the normal $\alpha$ manganese by heat treatment was unsuccessful, for after heating *in vacuo* for 24 hours at 120° no change occurred. At 150° it was entirely converted into the $\beta$ modification, the single broad line giving place to the normal $\beta$ pattern. On quenching from 900° some oxidation occurred, but the bulk of the

material was found to be of the $\gamma$ type, no evidence of the presence of the $\beta$ form being obtained. The spacings of this film are given in Table III. The oxide lines were all identified by comparison with another film obtained from a completely oxidized specimen. This gives a photograph exactly like that from NiO, both with regard to the positions of the lines and their intensities. It is therefore MnO. The structure is of the rock-salt type $a = 4{\cdot}45$ Å. *

TABLE III.

| Spacing. Å. | Substance. | Reflecting plane. | Side of unit cell. Å. |
|---|---|---|---|
| 2·575 | MnO | 111 | 4·460 |
| 2·229 | MnO | 200 | 4·458 |
| 2·114 | Mn$\gamma$ | | |
| 2·009 | Mn$\gamma$ | | |
| 1·916 | Mn$\gamma$ | | |
| 1·577 | MnO | 220 | 4·460 |
| 1·339 | MnO | 311 | 4·451 |
| 1·286 | MnO | 222 | 4·454 |
| 1·245 | Mn$\gamma$ | | |
| 1·221 | Mn$\gamma$ | | |
| 1·186 | Mn$\gamma$ | | |
| 1·166 | Mn$\gamma$ | | |
| 1·113 | MnO | 400 | 4·452 |

It has now been established that specimen H, obtained electrolytically, behaves quite like any other specimen of the metal when submitted to heat treatment. It was hoped to convert $\beta$ manganese obtained in this way back to the $\alpha$ modification, but no success has been attained. It seems probably that the transition temperature $\alpha \rightleftharpoons \beta$ is very low, and that the $\beta$ form will remain in a metastable form indefinitely since the velocity of change is so small. Perhaps some catalyst might hasten the transformation.

### 5. *Conclusion.*

The original objects of the investigation, which were to determine the structure of manganese and to investigate the possibility of allotropy of the elements, has not yet been completely attained; but the results so far obtained seem of sufficient importance and interest to justify publication at this stage. The patterns given by the $\beta$ and $\gamma$ forms are apparently impossible to reconcile with any but the lowest classes of crystal symmetry. Measurements made from

* See G. R. Levi, *Zeit. für Kristall.* lxi. p. 557 (1925).

selected films are given in Table IV. Column 1 gives the mean spacings of four specimens of $\beta$ manganese, and column 3 of five specimens of the $\gamma$ form. Column 5 shows the spacings obtained by Young *, for comparison. This is typical of all specimens containing mixtures of $\beta$ and $\gamma$, and would be in equilibrium about 750° †.

Table IV.

| $\frac{d}{n}$ ($\beta$Mn). | Intensity. | $\frac{d}{n}$ ($\gamma$Mn). | Intensity. | $\frac{d}{n}$ (Young). | Intensity. |
|---|---|---|---|---|---|
| 2·083 | v.s. | 2·086 | v.s. | 2·08 | 8 |
| | | 1·977 | v.s. | 1·97 | 4 |
| 1·886 | m | 1·886 | s | 1·88 | 4 |
| 1·807 | m–w | | | 1·80 | 1 |
| 1·737 | m | | | 1·74 | 2 |
| | | 1·676 | w–m | 1·67 | 1 |
| | | 1·481 | w–m | 1·48 | 2 |
| | | 1·404 | w | 1·41 | 2 |
| 1·341 | v.w. | | | | |
| | | 1·329 | v.w. | | |
| 1·283 | w–m | | | | |
| 1·256 | w–m | | | | |
| | | 1·234 | s | 1·23 | 4 |
| 1·212 | s | 1·213 | w | 1·21 | 4 |
| 1·190 | w | | | | |
| 1·169 | w | 1·169 | s | 1·17 | 4 |
| | | 1·149 | w | | |
| 1·131 | w | | | 1·12 | 2 |
| 1·098 | w | | | 1·10 | 2 |
| | | 1·064 | m-w | | |
| 1·049 | m–w | 1·049 | m | 1·05 | 2 |
| | | 1·031 | m-w | | |

v.s. = very strong; s = strong; m = moderate; w = weak; v.w. = very weak.

The lack of large spacings appears to indicate that the unit cell contains very few atoms, and this is further borne out by the comparatively small number of lines on the film. Some very simple monoclinic or orthorhombic structure would explain these facts. In the absence of adequate crystallographic data, very little more can be done until single crystals are obtained. An attempt is now being made to produce them. Attempts will also be made shortly to obtain the form by other methods probably colloidal, for

* *Loc. cit.*

† Seigfried von Olhausen in a recent paper has obtained a film by the use of chromium radiation, which is similar to Young's film, and without considering the possibility of his specimen being a mixture of two allotropes has ascribed to it a cubic structure containing 20 atoms to the unit cell. The present considerations appear to throw some doubt upon this result. (*Zeits für Kristall.* lxi. p. 463, 1925.)

the electrolytic method has the disadvantage that the product always contains hydrogen, so that it is impossible to be quite sure that we are not dealing with a hydride.

The allotropy of manganese has been established beyond doubt, but the attempt to find a definite transition point for the $\beta \rightleftharpoons \lambda$ transformation was quite unsuccessful. In fact, it appears that these two forms may co-exist over a wide range of temperatures. This is a remarkable phenomenon shown by no other metal, and some caution must be observed in interpreting the results. The system $\beta$ manganese + $\gamma$ manganese + vapour must be invariant if only one component is present, and would therefore have a definite transition temperature. It appears, however, that the system is univariant, and therefore requires two components. We are led to the conclusion that either the manganese was not sufficiently pure, or there are two kinds of manganese atoms or molecules.

In order to settle this point, further experiments will be made using specially purified specimens. A determination of the change in resistivity over the range 650° to 850° will be made, and X-ray powder photograms will be obtained while the specimen is heated to 750°.

This peculiar behaviour of manganese has an important bearing on Smits's Theory of Allotropy *. It may be possible that there is an analogy for this behaviour in the case of the so-called red modification of phosphorus, which is almost invariably a mixture of violet and white phosphorus.

This allotropy of manganese has a further bearing on the problem of magnetism. It has already been pointed out that, in the opinion of the author, allotropy is closely associated with the peculiar magnetic properties of the Heusler alloys. It seems probable from the present investigation that a more intimate type of allotropy than that involved by a mere change in crystal structure may occur. A change analogous to the transformation of $\alpha$ to $\beta$ iron, which only involves the interior of the atom, would satisfy the facts. This hypothesis will be tested by experiments on alloys.

The author is indebted to Prof. Bragg for his continuous help during the progress of this work; also to Mr. A. P. M. Fleming, C.B.E., M.Sc.(Tech.), Director of Research of Metropolitan-Vickers Electrical Co. Ltd., for suggesting this investigation, for his assistance during its progress, and

* A. Smits, 'Theory of Allotropy,' Part II. Chap. I.

for permission to publish the results. The work was carried out in the Physical Department of the University. The author's thanks are also due to Mr. A. G. Lobley, of the Electro-Chemical Department of the University, for co-operation in electro-deposition ; to Mr. D. H. Bangham for advice on the physical-chemical problems involved ; and to the Metallurgical Department for the loan of a furnace.

*Summary.*

1. An investigation of the crystal structure of manganese has led to the discovery af the allotropy of the element.

2. Two of the three allotropes are normally present in commercial manganese, and have been isolated and photographed by the X-ray powder method. It is proposed to called them $\beta$ and $\gamma$ manganese.

3. The $\beta$ form is stable within the range 150° to 850°, and the $\gamma$ form from 650° upwards. Within the region 650° to 850° both forms are stable, and the element here appears to show the phenomenon of isodynamic allotropy, an equilibrium mixture of the two allotropes corresponding to each temperature.

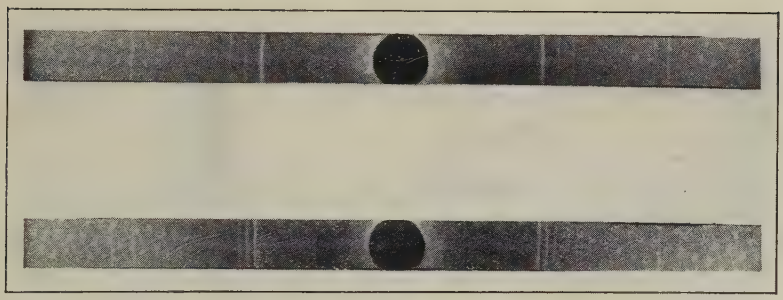
4. The third allotrope, which has so far only been obtained electrolytically, may be regarded either as a face-centred tetragonal structure with axial ratio $a : c = 1 : 0{\cdot}9445$, or as a body-centred tetragonal structure with axial ratio 1·34 : 1. It is therefore intermediate between a body-centred and face-centred cube. It is apparently only stable at quite low temperatures.

5. On heat treatment electrolytic manganese ($\alpha$ manganese) is converted into the $\beta$ and $\gamma$ forms, but the change does not appear to be reversible.

*Note added Oct. 8th.*—Since this communication was forwarded to the Philosophical Magazine a note has appeared in the *Zeitschrift für Physik* which covers roughly the same ground as the present paper (Arne Westgren and G. Phragmén, "Zum Kristallbau des Mangans," *Zeit. für Phys.* xxxiii. p. 777 (1925)). In agreement with the present results, the authors find that manganese has three allotropic forms. The authors denote the two common forms, referred to here as $\beta$ and $\gamma$, by the names $\alpha$ and $\beta$ respectively, and consider that they are cubic with 56 and 20 atoms to the unit cell. The precise arrangement of the atoms was not decided. The tetragonal modification obtained electrolytically, here referred to as the $\alpha$ form, is there denoted by the name of $\gamma$ manganese.

)
anese.

)
anese.



## CXI. *The Critical Increment of Chemical Reactions.*

*By* William Edward Garner *.

In a previous paper (Phil. Mag. vol. xlix. p. 463, 1925) the suggestion was made that the probability of a collision between active molecules yielding the reaction products is not unity. In the case of a bimolecular reaction,

$$A'+B' \underset{b}{\overset{a}{\rightleftharpoons}} \begin{matrix} AB' \\ \text{or} \\ CD' \end{matrix} \underset{d}{\overset{c}{\rightleftharpoons}} C'+D+Q, \quad . \quad . \quad . \quad (1)$$

the probability, $k_c/(k_c+k_b)$, is the fraction of the complexes AB′, formed from the active molecules A′ and B′, which break down to give C′ and D′. A similar suggestion, of which the author was unaware at the time, had previously been made by Herzfeld (*Z. Physik*, vol. viii. p. 135, 1922), based on the assumption that chemical reaction between active molecules cannot occur unless within the duration of collision the energy of reaction is removed by a third molecule. The author's view has been criticised by Mr. Hinshelwood (Phil. Mag. vol. l. p. 360, 1925), who concludes that the experimental evidence shows that this probability, especially in the case of irreversible reactions, is of the order unity. The experimental evidence to which he refers is confined to the three reactions, $2HI \rightleftharpoons I_2+H_2$, $2N_2O \rightleftharpoons 2N_2+O_2$, and $2Cl_2O \rightleftharpoons 2Cl_2+O_2$, for which there is agreement between the values of the Arrhenius constant, $A$, calculated, on the one hand, from the temperature coefficient of the experimental velocity constant, $k$, and, on the other hand, from this reaction constant with the aid of the classical kinetic theory (W. C. McC. Lewis, Trans. Chem. Soc. vol. cxiii. p. 474, 1918; Dushman, J. A. C. S. vol. xliii. p. 410, 1921; Hinshelwood and Hughes, vol. cxxv. p. 1842, 1924). The agreement is within experimental error.

An examination of the two methods shows that although they yield the same result for $A$, this concordance would not be expected to throw any light on the nature of the probability, $k_c/(k_c+k_b)$.

Assuming the mechanism illustrated by equation (1) and the Maxwell distribution law, it can be shown that the energy of activation

$$q_A+q_B=-RT(\log k_a-\text{const}-0{\cdot}5 \log T), \quad . \quad . \quad (2)$$

where $k_a$ is the velocity constant of complex formation, $q_A$ and $q_B$ are the energies required to activate a gram mol.

* Communicated by the Author.

of the molecules A and B respectively, and the constant contains the diameters and masses of the molecules taking part in the reaction. Dushman (*loc. cit.*) instead of $k_a$ employed $k_1$, the experimental velocity constant, to calculate $q_A + q_B$. Since $\log k_1 = \log k_a + \log\{k_c/(k_c+k_b)\}$, his calculated value will be in error by $-RT \log \{k_c/(k_c+k_b)\}$.

In the author's previous paper, assuming equation (1), it was shown that

$$(q_A + q_B)/RT^2 - A/RT^2 = d \log\{k_c/(k_c+k_b)\}/dT, \quad . \quad (3)$$

whence

$$(q_A + q_B)/RT - A/RT = \log\{k_c/(k_c+k_b)\} + i.$$

If $i$ is small or zero then the two methods should yield the same value for the energy of activation, which will be too small by $RT \log\{k_c/(k_c+k_b)\}$. Thus the agreement between the two methods cannot safely be taken as indicating that the Arrhenius constant is the true energy of activation of the reaction nor that the probability, $k_c/(k_c+k_b)$, is approximately unity. Further, Bodenstein, Lütkemeyer, and Müller (*Z. Elektrochemie*, vol. xxx. p. 416, 1924; *Z. Physikal. Chem.* vol. cxiv. p. 234, 1924), from a study of the thermal and photochemical reactions between hydrogen and bromine have deduced that in the reaction, $Br + Br \rightleftharpoons Br_2$, only 1/750 of the collisions between the atoms are fruitful, although bromine in the atomic form is normally assumed to be in the active state. For $H + H \rightleftharpoons H_2$, the probability of combination is even smaller (*Z. Elektrochemie*, vol. xxxi. p. 349, 1925).

With regard to the further criticism that $k_c/(k_c+k_b)$ cannot vary with temperature since active molecules are specified to possess the same energy independent of temperature, it should be remembered that even if the activity consist in the possession of a quantum of internal energy by the active molecules, the average energy of a complex formed by collision will increase with temperature. The average kinetic and unquantized internal energy of the active molecules will increase with temperature in accordance with Maxwell's distribution law. The relative rate of increase of the fraction of molecules with energy $E$ to $E+dE$ is the greater the larger the value of $E$. Whether or not this increase of the kinetic and unquantized internal energy of the active molecules will influence the value of $k_c/(k_c+k_b)$ is a matter for experiment to decide. The work of Bodenstein on bromine dissociation would appear to indicate that the effect is small, although the lack of accuracy in his values

for the probability of combination of bromine atoms leaves the question open.

It is possible to suggest another method by which the view may be tested which is based on a knowledge of the equilibrium constants for bimolecular reactions. If

$$q_A,\ q_B,\ q_C, \text{ and } q_D$$

be independent of temperature, as was tacitly assumed in the previous paper, then at the absolute zero

$$q_A+q_B-q_C-q_D=Q_0.$$

The equilibrium constant, $K=k_ak_c/k_dk_b$,

$$\therefore\quad d\ (\log k_a/k_d+\log k_c/k_b)/dT=-Q/RT^2,$$

where Q is the heat of reaction at any temperature,

but $\quad d\log(k_a/k_d)/dT=-Q_0/RT^2$ (see previous paper),

$$\therefore\quad d\log(k_c/k_b)/dT=-(Q-Q_0)/RT^2, \qquad (4)$$

or $\quad \log(k_c/k_b)=-(Q-Q_0)/RT+\text{const.}$

Since in equation (4) $Q-Q_0$ is a function of temperature, it follows that the probability $k_c/(k_c+k_b)$ varies with temperature.

The Sir William Ramsay Inorganic and
Physical Chemistry Laboratories,
University College, London.
Sept. 10th, 1925.

---

CXII. *On the Torsion of Hollow Oval Prisms.* *By* M. S. Ahmed, *of the Engineering Department, Osmaniah University of Hyderabad, Deccan* *.

## 1. Introduction.

1. THE general solution of the problem of the Torsion of Oval Tubes was given by Batho †, who obtained formulæ for strength and stiffness of infinitely thin prismatic

* Communicated by Prof. Cyril Batho, D.Sc.
† 'Engineering,' vol. 102 (1916).

tubes whatever their shape and whether the infinitely small thickness is uniform or not.

Later on valuable contributions to the problem of torsion were made by G. I. Taylor and A. A. Griffiths *.

Batho's formulæ are accurate for tubes of infinitesimal thickness, but may be slightly in error for the tubes of finite thickness mainly used in engineering structures. The object of this investigation is to establish formulæ for the torsional stiffness of uniform elliptic tubes likely to be made in practice, and to estimate the correction due to thickness necessary in applying Batho's formulæ.

Commercial tubes are generally of uniform gauge, *i. e.* of constant thickness, but no mathematical solution of the torsional problem of non-circular tubes of uniform finite thickness has ever been obtained.

De St. Venant † has treated the case of tubes bounded by similar ellipses. The fundamental theory for tubes bounded by confocal ellipses is given by Love ‡, but no solution is given. Now a tube bounded by similar and similarly situated ellipses is thickest at the ends of the major axis and a tube bounded by confocal ellipses is thickest at the ends of the minor axis, so that if the error introduced by using Batho's formula in each of these cases can be found, it is practically certain that the error introduced by applying the formula to an elliptic tube of uniform thickness will lie between the errors in the two extreme cases.

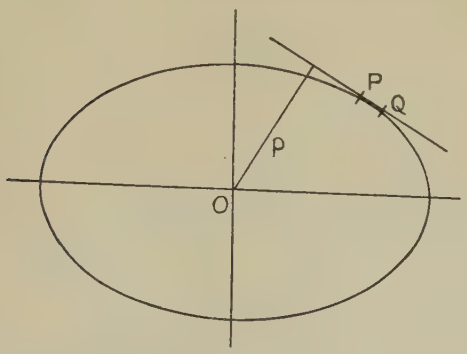
It is therefore proposed to obtain exact formulæ for the stiffness of tubes bounded by similar and similarly situated ellipses and for tubes bounded by confocal ellipses. Approximate formulæ will then be established for these two cases by Batho's method and error curves plotted for various values of $\frac{B}{A}$, where B is the area enclosed between the inner and outer boundaries and A is the over-all area. These results will be used to estimate a mean value for the error in the case of uniform tubes such as are used in practice.

* "The Determination of Stresses by Means of Soap Films," by G. I. Taylor, see 'The Mechanical Properties of Fluids,' Chap. vii.

† Pp. 333–352, St. Venant's original memoir: *Mémoire sur la Torsion de Prismes*, read to the French Academy in 1853 and published in *Mémoires des Savants étrangers de l'Académie des Sciences de Paris*, vol. xiv. (1855).

‡ 'Mathematical Theory of Elasticity,' 3rd edition, p. 325.

## 2. Tubes of Infinitesimal Thickness.




Thickness at any point P $= t$ inches, $t$ is not necessarily uniform round the circumference.
Area enclosed = A sq. ins.
Circumference = S inches.
Modulus of Rigidity = N lb. per sq. in.
Torque applied = T lb. inches.
Shear at any point P = $q$ lb. per sq. in.
Angle of twist per inch length of tube = $\tau$ radians.
Torsional stiffnes of tube = J inch$^4$ units.
So that $T = \tau NJ$.

From equilibrium of a small element PQ of the tube $qt$ is constant round the tube.

From moments about O, the axis of torsion

$$T = \int pqtds = qt \int pds = 2Aqt,$$

or
$$q = \frac{T}{2At} \quad \ldots\ldots\ldots\ldots \quad (1)$$

gives the shear stress on any section of thickness $t$.

Now consider the strain energy stored in an inch length of tube; it can easily be shown that it is equal to $\frac{1}{2}\frac{q^2}{N}$ per unit of volume.

$$\tfrac{1}{2}T\tau = \tfrac{1}{2}\int \frac{q^2}{N} tds,$$

$$TN\tau = qt\int qds = q^2t^2\int \frac{ds}{t},$$

but
$$T = NJ\tau,$$

$$J = \frac{4A^2}{\int \frac{ds}{t}} \quad \ldots\ldots\ldots\ldots \quad (2)$$

gives the torsional stiffness of the tube.

Hence for a tube of uniform thickness $t$, the stiffness

$$J = \frac{4A^2t}{S}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2\,a)$$

The formulæ (1) and (2) are due to Batho, who found them in a slightly different way. The procedure adopted here is perhaps more elegant

It may be noticed that (1) is true also for tubes of finite thickness if $q$ is defined as the average shear stress across a section of thickness $t$ and A is the mean area enclosed.

But the shear may vary sharply across the section, for instance at the ends of the major axis of a tube bounded by confocal ellipses, so that the average shear may be much below the maximum, and it would be rash to use (1) for commercial tubes without further investigation.

Formula (2) has not been proved for tubes of finite thickness, because it has been assumed in the proof that

$$\int q\,ds = qt\int \frac{ds}{t},$$

this means that $t$ is constant all round the tube. In reality $\int q\,dt$ is constant and $qt$ is not equal to $\int q\,dt$ unless $t$ is infinitely small. Hence (2) should not be used for commercial tubes until an estimate of the probable error is formed.

Since (1) and (2) can be easily calculated graphically for any tube if the section is given, they are of great practical value if a simple correction for error can be made.

## 3. Exact Determination of the Stiffness of Elliptical Tubes of Finite Thickness.

Let over-all area $=$A sq. in.

Area enclosed between the inner and outer boundaries $=$B sq. in.

Fineness Ratio, *i. e.* Ratio of greatest to least diameter of outer boundary $=f$.

A, B, and $f$ can be found at once by a draughtsman from a drawing of the tube, we will therefore work in terms of these quantities as far as possible.

### (a) *Tubes bounded by Similar and Similarly Situated Ellipses.*

$a_0$, $b_0$, $a_1$, $b_1$, are the semi-major and minor axes of the outer and inner ellipses respectively. $Js$ is the torsional stiffness of the tube.

De St. Venant * was the first to treat this problem. In our notation

$$\dagger J = \iint \left( x^2 + y^2 - x\frac{d\psi}{dx} - y\frac{d\psi}{dy} \right) dx\, dy$$

and $$\ddagger \psi = \frac{1}{2}\frac{a^2 - b^2}{a^2 + b^2}(x^2 - y^2),$$

or $$J = \frac{2}{a^2 + b^2}\iint (b^2x^2 + a^2y^2) dx\, dy,$$

but $\iint x^2\, dx\, dy$ = moment of inertia of ellipse about $y$ axis

$$= \pi ab \cdot \frac{a^2}{4};$$

similarly $\iint y^2\, dx\, dy = I$ about $x$ axis.

$$J_0 = \frac{\pi a^3 b^3}{a^2 + b^2} \text{ for the whole ellipse.}$$

Subtracting $J_i$ for the inner ellipse, we get

$$\S\ J = J_0 - J_i = \frac{\pi {a_0}^3 {b_0}^3}{{a_0}^2 + {b_0}^2} - \frac{\pi {a_1}^3 {b_1}^3}{{a_1}^2 + {b_1}^2},$$

since $a_0 = f b_0$ and $a_1 = f b_1$,

$$J = \frac{\pi f^3}{(f^2 + 1)}({b_0}^4 - {b_1}^4)$$

and $$\frac{\pi J}{B(2A - B)}\left(f + \frac{1}{f}\right) = 1. \quad . \quad . \quad . \quad . \quad (3)$$

(b) *Exact Determination of the Stiffness of Tubes bounded by Confocal Ellipses.*

$a_0$, $b_0$, $a_1$, $b_1$ have the same significance as before. $J_c$ is the torsional stiffness of the tube. The torsion function for this problem is given by Love ‖, and we can deduce the expression for stiffness.

* Kelvin & Tait's 'Natural Philosophy,' Part 2, p. 246, paragraph 707.

† Love's 'Elasticity,' 3rd edition, p. 317.

‡ *Ibid.* p. 322.

§ It should be noticed in passing that this step is legitimate only if the inner boundary is a "line of stress" for a solid shaft of the same outer boundary. This is true for similar and similarly situated ellipses (including concentric circles as a special case) but not for confocal ellipses, nor for elliptic tubes of uniform thickness. This point, however, was first noticed by De St. Venant. See Love's 'Elasticity,' 3rd edition, article 221 (*b*).

‖ 'Elasticity,' 3rd edition, p. 325.

In our notation the expression for torsional stiffness is as follows :—

$$^{*}\frac{4J_c}{\pi} = a_0b_0(a_0^2+b_0^2) - a_1b_1(a_1^2+b_1^2) - (a_0^2-b_0^2)^2\frac{a_1b_0-a_0b_1}{a_0a_1-b_0b_1} \quad . \quad . \quad (4)$$

For the numerical work that follows it is convenient to use the following transformation :—

Let $f = \sec\theta$,

$b_1 = b_0 \tan\theta \tan\alpha$.

Then, since by a property of confocal ellipses

$$a_1^2 - b_1^2 = a_0^2 - b_0^2,$$

we have $a_0 = b_0 \sec\theta$,

$a_1 = b_0 \tan\theta \sec\alpha$,

$b_1 = b_0 \tan\theta \tan\alpha$,

$$\frac{A}{\pi b_0^2} = \sec\theta,$$

and $$\frac{B}{\pi b_0^2} = \sec\theta - \tan^2\theta \tan\alpha \sec\alpha,$$

$$\frac{4J_c}{\pi b_0^4} = \sec\theta(\sec^2\theta+1) - \tan^4\theta \tan\alpha \sec\alpha\,(1+2\tan^2\alpha) - \tan^4\theta\frac{\cos\theta-\sin\alpha}{1-\sin\alpha\cos\theta} \quad . \quad (5)$$

It will be seen that from (5) we can get the torsional stiffness of any tube bounded by confocal ellipses. But in proceeding further it is more convenient to calculate the *non-dimensional* quantity

$$\frac{\pi J_c}{B(2A-B)}\left(f+\frac{1}{f}\right).$$

The non-dimensional character of this quantity makes it easy to be manipulated whatever the units of the quantities are.

The non-dimensional quantity

$$\frac{\pi J_c}{B(2A-B)}\left(f+\frac{1}{f}\right)$$

has been calculated by giving suitable values to $\theta$ and $\tan\alpha$ for several values of $\frac{B}{A}$ and for the following values of $f$:—

$$f=1, \qquad f=2, \qquad f=3{\cdot}5, \qquad f=\infty.$$

* Greenhill, Quarterly Journal of Mathematics, 1879, p. 233.

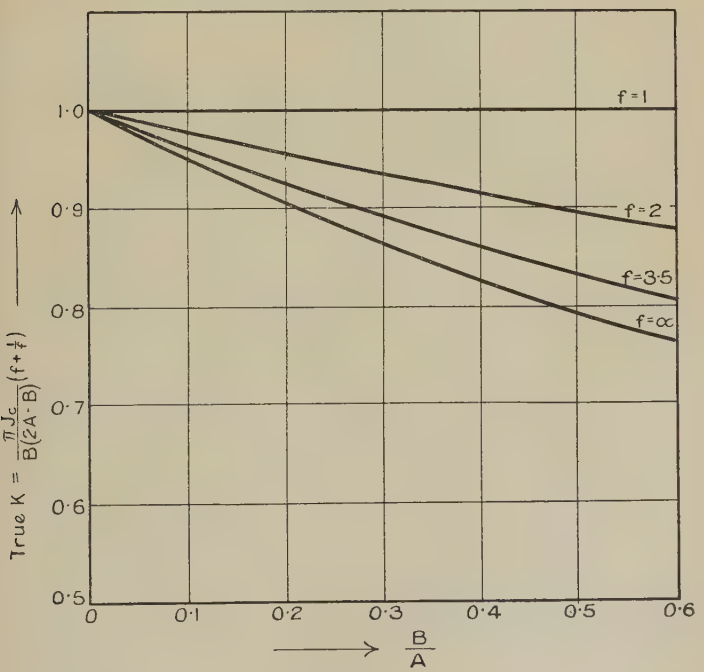
The graphs are shown in fig. 1.

It will be seen that for values of $\frac{B}{A}$ less than $\frac{1}{2}$ the curves are nearly straight lines, and the formula

$$\frac{\pi J_c}{B(2A-B)}\left(f+\frac{1}{f}\right)=1-(\cdot 46)\left(1-\frac{1}{f}\right)\frac{B}{A} \quad . \quad (6)$$

is correct to within 2 per cent. for all values of $\frac{B}{A}$ less than $\frac{1}{2}$ and for all values of $f$ between 1 and $\infty$.

Fig. 1.




For lower values of $\frac{B}{A}$ and $f$ the approximation is very much closer. For metal tubes $f$ is very seldom as large as 3 and $\frac{B}{A}$ is usually less than $\frac{1}{2}$. Hence for tubes whose dimensions are likely to be of practical interest the formula (6) will usually be correct to 3 figures. But it will be

remembered that for a tube bounded by similar ellipses

$$\frac{\pi J}{B(2A-B)}\left(f+\frac{1}{f}\right)=1. \quad . \quad . \quad . \quad . \quad (3)$$

Equations (3) and (6) are of considerable interest as they refer to extreme cases.

## 4. Approximate Determination of the Stiffness of Elliptical Tubes of Finite Thickness by Batho's Method.

In attempting to apply Batho's formulæ (1) and (2) to tubes of finite non-uniform thickness, we shall define the thickness $t$ and the mean area $A_m$ as follows :—

The thickness is the perpendicular distance between two parallel tangents to the inner and outer boundaries of the tube. The mean curve is the envelope of a straight line parallel to two parallel tangents and midway between them. S is measured along the circumference of the mean curve and $A_m$ is the area of the mean curve.

### (a) *Tubes bounded by Similar and Similarly Situated Ellipses.*

With the previous notation, the mean curve is also a similar and similarly situated ellipse with semi-axes $\frac{1}{2}(a_0+a_1)$, $\frac{1}{2}(b_0+b_1)$. The tangents at the points $(a_0\cos\theta,\ b_0\sin\theta)$, $(a_1\cos\theta,\ b_1\sin\theta)$ are parallel, and

$$t=\frac{a_0b_0}{\sqrt{a_0^2\sin^2\theta+b_0^2\cos^2\theta}}-\frac{a_1b_1}{\sqrt{a_1^2\sin^2\theta+b_1^2\cos^2\theta}}$$

for the mean curve

$$\frac{ds}{d\theta}=\frac{1}{2}\left(1+\frac{a_1}{a_0}\right)\sqrt{a_0^2\sin^2\theta+b_0^2\cos^2\theta}$$

$$\int\frac{ds}{t}=\frac{1}{2}\frac{(a_0+a_1)}{a_0b_0(a_0-a_1)}\int_0^{\frac{\pi}{2}}4(a_0^2\sin^2\theta+b_0^2\cos^2\theta)d\theta$$

$$=\frac{\pi}{2}\frac{(a_0+a_1)(a_0^2+b_0^2)}{a_0b_0(a_0-a_1)}.$$

From (2)

$$J_B=\frac{4A_m^2}{\int\frac{ds}{t}}=\tfrac{1}{2}\pi\frac{(a_0^2-a_1^2)(b_0+b_1)^2a_0b_0}{(a_0^2+b_0^2)}$$

$$=\tfrac{1}{2}\pi\frac{f}{1+f^2}\cdot\frac{1}{f^2}(a_0^2-a_1^2)(a_0+a_1)^2,$$

$$\frac{\pi J_B}{B(2A-B)}\left(f+\frac{1}{f}\right)=\frac{(a_0+a_1)^2}{2(a_0^2+a_1^2)},$$

which is less than 1, so that for a tube of finite thickness bounded by similar ellipses *Batho reads low.*

$$1-\frac{J_B}{J_s}=\frac{1}{2}-\frac{\sqrt{1-\frac{B}{A}}}{2-\frac{B}{A}}. \quad . \quad . \quad . \quad . \quad (7)$$

Hence the percentage by which Batho reads low for stiffness of a tube bounded by similar ellipses is

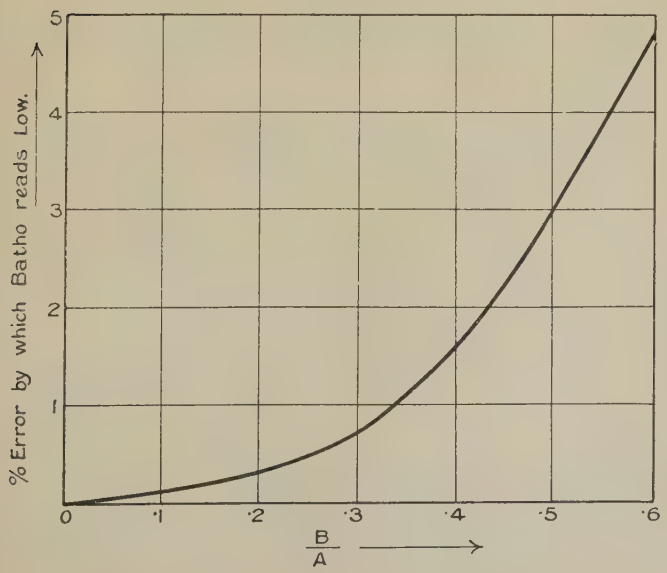
$$50\left\{1-\frac{\sqrt{1-\frac{B}{A}}}{1-\frac{B}{2A}}\right\}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

*e. g.* if $\frac{B}{A}=\cdot5$, this is 2·9 per cent.

| $\frac{B}{A}=$ | 0 | ·2 | ·4 | ·6 | ·8 | 1·0 |
|---|---|---|---|---|---|---|
| Per cent. error = | 0 | ·3 | 1·6 | 4·8 | 12·7 | 50 |

These results are shown graphically in fig. 2.

Fig. 2.



(b) *Tubes bounded by Confocal Ellipses.*

In this case the mean curve which is not an ellipse has for its tangential polar equation

$$2p = \sqrt{a_0^2\cos^2\psi + b_0^2\sin^2\psi} + \sqrt{a_1^2\cos^2\psi + b_1^2\sin^2\psi}, \quad . \quad (9)$$

where $p$ and $\psi$ have their usual significance, and the thickness

$$t = \sqrt{a_0^2\cos^2\psi + b_0^2\sin^2\psi} - \sqrt{a_1^2\cos^2\psi + b_1^2\sin^2\psi}$$

from (2)

$$J_B = \frac{4A_m^2}{\int\frac{ds}{t}}.$$

By a property of confocals

$$a_0^2 - b_0^2 = c^2 \text{ say } = a_1^2 - b_1^2$$

and

$$a_0^2 - a_1^2 = b_0^2 - b_1^2 = c_1^2 \text{ say,}$$

$$J_B = C_1^2 A_m.$$

By a well-known formula for closed ovals

$$A_m = \frac{1}{2}\int\left\{p^2 - \left(\frac{dp}{d\psi}\right)^2\right\}d\psi. \quad . \quad . \quad . \quad (10)$$

From (9)

$$2\frac{dp}{d\psi} = -\frac{c^2\sin\psi\cos\psi(2p)}{\sqrt{a_0^2\cos^2\psi + b_0^2\sin^2\psi}\ .\ \sqrt{a_1^2\cos^2\psi + b_1^2\sin^2\psi}}.$$

From (10)

$$A_m = \frac{1}{2}\int\left\{1 - \frac{c^4\sin^2\psi\cos^2\psi}{(a_0^2\cos^2\psi + b_0^2\sin^2\psi)(a_1^2\cos^2\psi + b_1^2\sin^2\psi)}\right\}p^2$$

where $a_0^2\cos^2\psi + b_0^2\sin^2\psi = a_0^2 - c^2\sin^2\psi$

and $a_1^2\cos^2\psi + b_1^2\sin^2\psi = a_1^2 - c^2\sin^2\psi.$

$$A_m = \frac{1}{2}\int_0^{\frac{\pi}{2}}\Big[\Big\{1 - \frac{c^4\sin^2\psi\cos^2\psi}{(a_0^2 - c^2\sin^2\psi)(a_1^2 - c^2\sin^2\psi)}\Big\}$$
$$\times\{(a_0^2 - c^2\sin^2\psi) + (a_1^2 - c^2\sin^2\psi)$$
$$+ 2\sqrt{a_0^2 - c^2\sin^2\psi}\ .\ \sqrt{a_1^2 - c^2\sin^2\psi}\}\Big]d\psi, \quad (11)$$

and

$$\int_0^{2\pi}(11) = 4\int_0^{\frac{\pi}{2}}(11)$$

taken all round the oval, as there is symmetry about both axes.

Integrating some terms in (11), we get

$$\frac{1}{2}\int_0^{\frac{\pi}{2}} (a_0^2 - c^2\sin^2\psi + a_1^2 - c^2\sin^2\psi)\,d\psi$$

$$= \frac{\pi}{4}(a_0^2 + a_1^2 - c^2); \qquad (12)$$

$$\frac{1}{2}\int_0^{\frac{\pi}{2}} \left\{ \frac{c^4\sin^2\psi\cos^2\psi}{(a_0^2 - c^2\sin^2\psi)(a_1^2 - c^2\sin^2\psi)} \right\} \times \{(a_0^2 - c^2\sin^2\psi) + (a_1^2 - c^2\sin^2\psi)\}\,d\psi$$

$$= \frac{1}{2}\int_0^{\frac{\pi}{2}} \left\{ \frac{c^4\sin^2\psi\cos^2\psi}{(a_1^2 - c^2\sin^2\psi)} + \frac{c^4\sin^2\psi\cos^2\psi}{(a_0^2 - c^2\sin^2\psi)} \right\} d\psi. \qquad (13)$$

It can easily be shown that the first part of (13) is equal to

$$\frac{\pi}{4}(c^2 + 2b_1^2) - a_1 b_1 \left[ \tan^{-1} b_1 \frac{\tan\psi}{a_1} \right]_0^{\frac{\pi}{2}} = \frac{\pi}{4}(a_1 - b_1)^2.$$

Similarly the second part of (13) $= \frac{\pi}{4}(a_0 - b_0)^2$,

or $$(13) = \frac{\pi}{8}\{(a_0 - b_0)^2 + (a_1 - b_1)^2\}.$$

It has already been shown that

$$(12) = \frac{\pi}{8}(a_0^2 + a_1^2 + b_0^2 + b_1^2).$$

The first part of $A_m$, *i. e.* (11) is $(12) - (13) = \frac{1}{4}(A + \overline{A - B})$.

Finally

$$\left.\begin{aligned} A_m = \tfrac{1}{4}(2A - B) + \int_0^{\frac{\pi}{2}} \sqrt{a_0^2 - c^2\sin^2\psi}\ .\ \sqrt{a_1^2 - c^2\sin^2\psi}\,d\psi \\ - \int_0^{\frac{\pi}{2}} \frac{c^4\sin^2\psi\cos^2\psi}{\sqrt{(a_0^2 - c^2\sin^2\psi)}\ .\ \sqrt{(a_1^2 - c^2\sin^2\psi)}}\,d\psi. \end{aligned}\right\} \qquad (14)$$

These integrals have been evaluated for certain finite values of $f$ such as $f=1$, $f=2$, $f=3{\cdot}5$ by means of approximate integration, but for the values of $f=\infty$ they present great mathematical difficulty on account of their non-uniformity of convergence. The following method, however, enables us accurately to evaluate them for $f=\infty$.

Let $$\left.\begin{aligned} b_0 &= \epsilon a_0 \\ \text{and} \quad b_1 &= \eta a_1 \end{aligned}\right\} \begin{aligned} \eta &< \epsilon \\ \epsilon &= \frac{1}{f}, \end{aligned}$$

neglecting $\epsilon^3$ and higher powers and so also $\eta^3$ and higher powers, we get on substitution in (14)

$$\tfrac{1}{4}(2\mathrm{A}-\mathrm{B}) = \frac{\pi}{4}(a_0^2\epsilon + a_1^2\eta), \quad . \quad . \quad . \quad (15)$$

and $$\int_0^{\frac{\pi}{2}} \sqrt{a_0^2 - c^2\sin^2\psi} \,.\, \sqrt{a_1^2 - c^2\sin^2\psi}\, d\psi$$

$$= \int_0^{\frac{\pi}{2}} a_0\cos\psi\{1+\tfrac{1}{2}\epsilon^2\tan^2\psi\} a_1\cos\psi\{1+\tfrac{1}{2}\eta^2\tan^2\psi\} d\psi$$

$$= \frac{\pi}{4} a_0 a_1 \{1 + \tfrac{1}{2}\epsilon^2 + \tfrac{1}{2}\eta^2\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$\int_0^{\frac{\pi}{2}} \frac{c^4 \sin^2\psi\cos^2\psi}{\sqrt{a_0^2 - c^2\sin^2\psi} \,.\, \sqrt{a_1^2 - c^2\sin^2\psi}} d\psi$$

$$= a_0 a_1 (1-\epsilon^2-\eta^2) \int_0^{\frac{\pi}{2}} \frac{\sin^2\psi\cos^2\psi}{\cos^2\psi + \frac{1}{2}(\epsilon^2+\eta^2)\sin^2\psi} d\psi. \quad (17)$$

Let us now consider

$$\int_0^{\frac{\pi}{2}} \frac{\sin^2\psi\cos^2\psi}{\cos^2\psi + \frac{1}{2}(\epsilon^2+\eta^2)\sin^2\psi} d\psi ;$$

this can be written in a more general form as

$$\int_0^{\frac{\pi}{2}} \frac{-\cos^4\psi + \cos^2\psi}{(p^2-q^2)\cos^2\psi + q^2} d\psi,$$

and is equal to

$$-\frac{\pi}{4}\frac{1}{p^2-q^2} + \frac{\pi}{2}\frac{p^2}{(p^2-q^2)^2}$$

$$-\frac{p^2q^2}{(p^2-q^2)^2}\int_0^{\frac{\pi}{2}} \frac{1}{p^2\cos^2\psi + q^2\sin^2\psi} d\psi.$$

Also

$$\int_0^{\frac{\pi}{2}} \frac{d\psi}{p^2\cos^2\psi + q^2\sin^2\psi} = \left[\frac{1}{pq}\tan^{-1}\frac{q\tan\psi}{p}\right]_0^{\frac{\pi}{2}} = \frac{\pi}{2pq}.$$

Hence

$$\int_0^{\frac{\pi}{2}} \frac{\sin^2\psi\cos^2\psi}{\cos^2\psi \cdot \frac{1}{2}(\epsilon^2+\eta^2)\sin^2\psi}\,d\psi = \frac{\pi}{4}\frac{1}{(p+q)^2}.$$

On making these substitutions in (17) we get

$$a_0a_1(1-\epsilon^2-\eta^2)\int_0^{\frac{\pi}{2}} \frac{\sin^2\psi\cos^2\psi}{\cos^2\psi+\frac{1}{2}(\epsilon^2+\eta^2)\sin^2\psi}\,d\psi$$
$$= a_0a_1\frac{\pi}{4}\{1-\sqrt{2(\epsilon^2+\eta^2)}+\tfrac{1}{2}(\epsilon^2+\eta^2).$$

Finally,

$$A_m = \frac{\pi}{4}\{a_0b_0+a_1b_1+\sqrt{2(a_1^2b_0^2+a_0^2b_1^2)}\}, \quad . \quad (18)$$

when $f=\infty$.

To plot the curve K against $\frac{B}{A}$, the expression for K is to be simplified and it is done as follows :—We have

$$\frac{\pi A_m(a_0^2-a_1^2)}{B(2A-B)}\cdot\left(f+\frac{1}{f}\right)=K,$$

or

$$K=\frac{\pi^2}{4}\left(f+\frac{1}{f}\right)(a_0^2-a_1^2)\left\{\frac{(a_0b_0+a_1b_1)+\sqrt{2(a_1^2b_0^2+a_0^2b_1^2)}}{\pi^2(a_0^2b_0^2-a_1^2b_1^2)}\right\}.$$

In the factor $\left(f+\frac{1}{f}\right)$ we only need retain $f$, as $\epsilon=\frac{1}{f}\to 0$, and may be neglected.

Putting $\left.\begin{matrix} b_0=\epsilon a_0 \\ b_1=\eta a_1 \end{matrix}\right\} f=\frac{1}{\epsilon}$

and $$K=\frac{1}{4\epsilon}(a_0^2-a_1^2)\left\{\frac{\epsilon a_0^2+\eta a_1^2+a_0a_1\sqrt{2(\epsilon^2+\eta^2)}}{(\epsilon^2a_0^4-\eta^2a_1^4)}\right.,$$

but $$a_0^2-a_1^2=b_0^2-b_1^2=\epsilon^2a_0^2-\eta^2a_1^2.$$

Hence $$a_1=a_0(1-\tfrac{1}{2}\epsilon^2+\tfrac{1}{2}\eta^2).$$

After some reduction we find

$$K=\frac{1}{4}\left\{1+\frac{\eta}{\epsilon}+\sqrt{2\left(1+\frac{\eta^2}{\epsilon^2}\right)}\right\}.$$

If we put $\frac{B}{A}=x$, it can easily be shown that

$$\frac{\eta}{\epsilon}=1-x \text{ approximately.}$$

Finally $K=\frac{1}{4}\{2-x+\sqrt{2(2-2\,.\,x+x^2)}\}$, where $x=\frac{B}{A}$.

The values of K for different values of $\frac{B}{A}$ are plotted in fig. 3 for values of $f=1$, $f=2$, $f=3{\cdot}5$, $f=\infty$, and the error curves for the same values of $f$ are plotted in fig. 4.

Fig. 3.

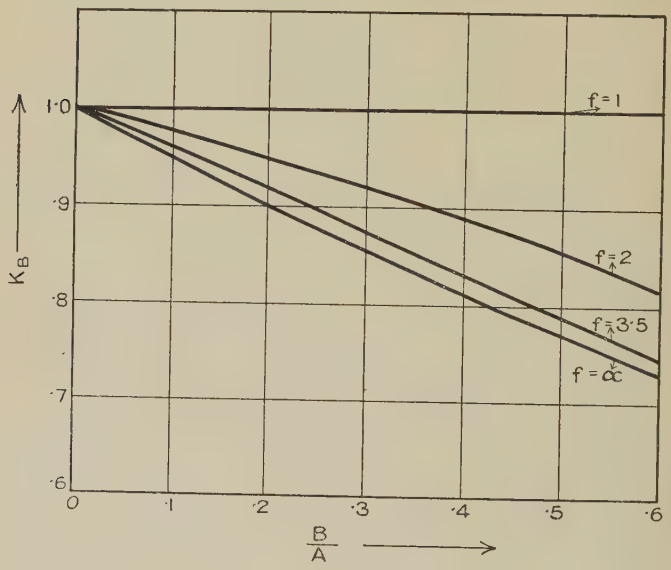
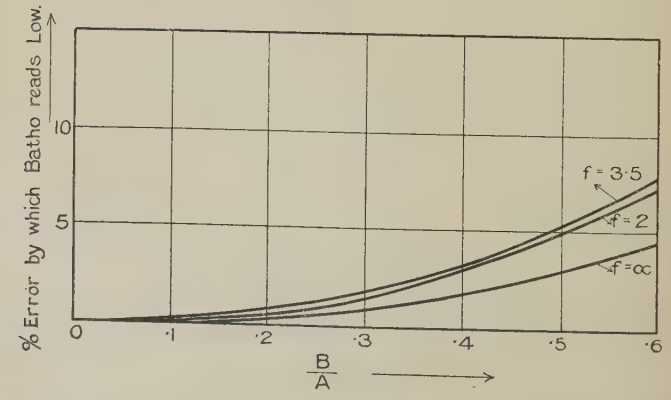



Fig. 4.




The various values are tabulated in the accompanying Tables.

## 5. Comparison of the Approximate and Exact Methods for Tubes of Finite Thickness.

For $f=2$.

| $\frac{B}{A}$ ..... = | 0 | ·25 | ·50 | 1·0 |
|---|---|---|---|---|
| True K, see fig. 1 = | 1 | ·946 | ·896 | ·857 |
| Batho's K, see fig. 3 = | 1 | ·938 | ·855 | ·662 |
| Difference ..... = | 0 | ·008 | ·041 | ·195 |
| Per cent. error $= \frac{100(K_{True}-K_B)}{K_{True}}$ = | 0 | ·845 | 4·575 | 22·753 |

For $f=3{\cdot}5$.

| $\frac{B}{A}$ ..... = | 0 | ·25 | ·50 | 1·0 |
|---|---|---|---|---|
| True K, see fig. 1 = | 1 | ·905 | ·830 | ·790 |
| Batho's K, see fig. 3 = | 1 | ·893 | ·787 | ·600 |
| Difference ..... = | 0 | ·012 | ·043 | ·190 |
| Per cent. error $= \frac{100(K_{True}-K_B)}{K_{True}}$ = | 0 | 1·325 | 5·180 | 24·050 |

For $f=\infty$.

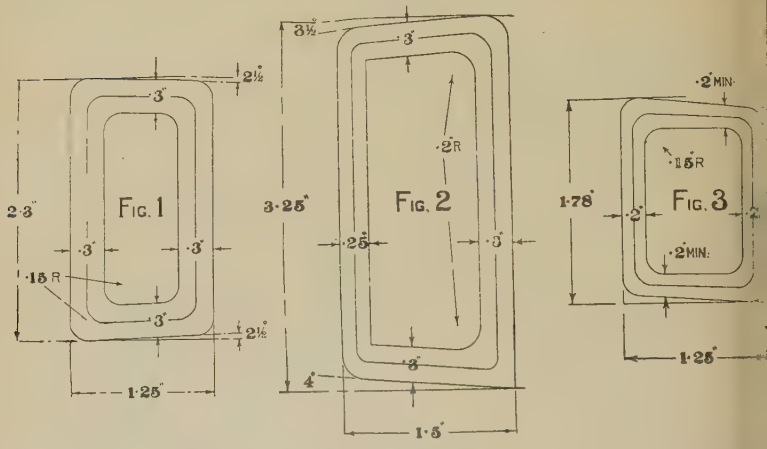
| $\frac{B}{A}$ ..... = | 0 | ·25 | ·50 | 1·0 |
|---|---|---|---|---|
| True K, see fig. 1 = | 1 | ·885 | ·793 | ·747 |
| Batho's K, see fig. 3 = | 1 | ·879 | ·770 | ·3535 |
| Difference ..... = | 0 | ·006 | ·023 | ·3935 |
| Per cent. error $= \frac{100(K_{True}-K_B)}{K_{True}}$ = | 0 | ·6779 | 2·900 | 52·677 |

## 6. Conclusion.

To conclude we infer that for any prismatic tubes of over-all sectional area A with central holes (area of metal section being B), Batho's construction for torsional stiffness reads *low* by $6\frac{B}{A}$ per cent., so long as $\frac{B}{A}$ is less than ·6, and the error in this statement does not exceed 1 per cent. for any tubes likely to occur in engineering practice, except for certain hollow wooden spars used in aircraft construction (see photographic figs. 1, 2, 3), for which the error may be as high, in extreme cases, as 3 per cent. *on the side of safety*; our formula in fact, for such extreme spars, always *underestimates* the stiffness, and this is a very valuable feature in aircraft design.

It is proposed later to investigate the case of a tube the

inner and outer boundaries being circles which are not concentric. The conjugate function for this case is given by Love *.




ELEVATOR SPAR — AUSTIN GREYHOUND

TOP AILERON — GREYHOUND

BOTTOM AILERON — GREYHOUND

Fig. 1.

| | | | |
|---|---|---|---|
| A | = | 2·802 square inches. | |
| $A_m$ | = | 1·842 | ,, ,, |
| $A_1$ | = | 1·066 | ,, ,, |
| $A-A_1=B=$ | | 1·736 | ,, ,, |
| $\frac{B}{A}$ | = | ·6195 | ,, ,, |

Fig. 2.

| | | | |
|---|---|---|---|
| A | = | 4·724 square inches. | |
| $A_m$ | = | 3·47 | ,, ,, |
| $A_1$ | = | 2·3300 | ,, ,, |
| $A-A_1=B=$ | | 2·394 | ,, ,, |
| $\frac{B}{A}$ | = | ·5068 | ,, ,, |

Fig. 3.

| | | | |
|---|---|---|---|
| A | = | 2·11 square inches. | |
| $A_m$ | = | 1·529 | ,, ,, |
| $A_1$ | = | 1·0492 | ,, ,, |
| $A-A_1=B=$ | | 1·0608 | ,, ,, |
| $\frac{B}{A}$ | = | ·5027 | ,, ,, |

It is possible that the error in applying Batho's construction may increase with the eccentricity of the hole or it may not. The investigation regarding eccentric holes may throw further light on this point.

Lastly, the author desires to express his indebtedness to Professor Cyril Batho, of the University of Birmingham, for valuable criticism and advice.

* 'Elasticity,' 3rd edition, p. 325.

CXIII. *Laplace's Equation and the Inversion of Coordinates.* *By* D. M. Wrinch, *M.A., D.Sc., Lecturer at Lady Margaret Hall, Oxford* *.

THE solution of the problems of Electrostatics, Hydrodynamics, and related branches of Mathematical Physics associated with a specific surface S depends, in the first place, on the discovery of curvilinear coordinates $(\xi, \eta, \zeta)$ such that the surface S belongs to one of the three families $\xi = \text{constant}$, $\eta = \text{constant}$, or $\zeta = \text{constant}$. Next, it is necessary to obtain a suitable solution of Laplace's equation

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0$$

in the form

$$V = f(\xi, \eta, \zeta),$$

and finally to apply the condition which has to be satisfied on the surface S given by (say) $\xi = \xi_0$.

Now, if the appropriate curvilinear coordinates have been discovered which give the surface in the form $\xi = \xi_0$, the introduction of the inverse coordinates

$$x' = k^2 x/r^2, \quad y' = k^2 y/r^2, \quad z' = k^2 z/r^2,$$

when any point whatever is taken as the centre of inversion, suggests the consideration of problems related to the surface S′ inverse to S. For this surface S′ will be given by $\xi = \xi_0$, and therefore the task of finding appropriate curvilinear coordinates for S′ has already been accomplished. It then remains to find a suitable solution of Laplace's equation

$$\frac{\partial^2 V'}{\partial x'^2} + \frac{\partial^2 V'}{\partial y'^2} + \frac{\partial^2 V'}{\partial z'^2} = 0$$

in the form

$$V' = g(\xi, \eta, \zeta),$$

and then to satisfy on S′ the condition which the particular problem under consideration requires.

Now it is in fact the case, as will be proved in the sequel, that if

$$V = f(\xi, \eta, \zeta)$$

is a solution of Laplace's equation for coordinates $(x, y, z)$, then

$$V' = \frac{k'}{r'} f(\xi, \eta, \zeta) = \frac{r}{k} f(\xi, \eta, \zeta)$$

is a solution of Laplace's equation for the coordinates $(x', y', z')$ inverse to $(x, y, z)$.

* Communicated by the Author.

This theorem, it is found, allows applications of a comprehensive character. For given any two surfaces S and S′, inverse to each other, the discovery of appropriate coordinates for S′ at once gives the appropriate coordinates for S and a general solution for the coordinates $(x', y', z')$, as, for example,

$$V' = \Sigma\Sigma\, P_n^m(\mu)\left\{a_n^m p_n^m(\zeta) + b_n^m q_n^m(\zeta)\right\}\cos(m\xi + \alpha_m)$$

for the oblate spheroidal coordinates defined by

$$z' = c'(\mu\zeta + \zeta_1),$$
$$x', y' = c'(1-\mu^2)^{1/2}(\zeta^2+1)^{1/2}\{\cos\xi, \sin\xi\}$$

at once furnishes a general solution

$$V = \left(\frac{k}{r'}, \frac{r'}{c'}\right)\Sigma\Sigma\, P_n^m(\mu)\left\{a_n^m p_n^m(\zeta) + b_n^m q_n^m(\zeta)\right\}\cos(m\xi + \alpha_m)$$

for the inverse coordinates

$$z, x, y = c[\mu\zeta + \zeta_1, (1-\mu^2)^{1/2}(\zeta^2+1)^{1/2}\{\cos\xi, \sin\xi\}] \times (1 + \zeta^2 + \zeta_1{}^2 - \mu^2 + 2\mu\zeta\zeta_1)^{-1/2}.$$

And evidently, if V′ satisfies a certain condition on the surface S′, V will satisfy a related condition on the surface S.

Kelvin's well-known geometrical treatment * of some electrostatic problems depends upon a particular case of this theorem, when, in fact, the potential V′ is constant over the conductor S′. But, plainly, this is a very mild application, for the theorem used in its full generality shows that the appropriate functions for problems associated with S′ are in fact also the appropriate functions for *all* the problems associated with S.

### *The Inversion of Coordinates.*

Suppose the orthogonal curvilinear coordinates $(\xi, \eta, \zeta)$ are given by the equations

$$\phi(x', y', z') = \xi,$$
$$\psi(x', y', z') = \eta,$$
$$\chi(x', y', z') = \zeta.$$

* *Cp.* 'Papers on Electrostatics and Magnetism' (Sir W. Thomson), (1872) xiv.

The elements of length normal to the surface, $\xi$, $\eta$, $\zeta =$ constant, are

$$dn_\xi = d\xi/h_\xi, \quad dn_\eta = d\eta/h_\eta, \quad dn_\zeta = d\zeta/h_\zeta$$

with

$$\frac{1}{h_\xi^2} = \left(\frac{\partial x}{\partial \xi}\right)^2 + \left(\frac{\partial y}{\partial \xi}\right)^2 + \left(\frac{\partial z}{\partial \xi}\right)^2$$

and similar relations for $\eta$ and $\zeta$. Laplace's equation takes the well-known form

$$\frac{\partial}{\partial \xi}\left(\frac{h_\xi}{h_\eta h_\zeta}\frac{\partial V}{\partial \xi}\right) + \frac{\partial}{\partial \eta}\left(\frac{h_\eta}{h_\zeta h_\xi}\frac{\partial V}{\partial \eta}\right) + \frac{\partial}{\partial \zeta}\left(\frac{h_\zeta}{h_\xi h_\eta}\frac{\partial V}{\partial \zeta}\right) = 0. \quad (1)$$

Consider now the coordinates $(x', y', z')$ inverse to $(x, y, z)$, given by

$$\frac{x'}{x} = \frac{y'}{y} = \frac{z'}{z} = \frac{r'}{r} = \frac{k^2}{r^2} = \frac{r'^2}{k^2}$$

with radius of inversion $k$. Then $(\xi, \eta, \zeta)$ are now given by the equations

$$\phi\left(\frac{kx'}{r'^2}, \frac{ky'}{r'^2}, \frac{kz'}{r'^2}\right) = \xi,$$

$$\psi\left(\frac{kx'}{r'^2}, \frac{ky'}{r'^2}, \frac{kz'}{r'^2}\right) = \eta,$$

$$\chi\left(\frac{kx'}{r'^2}, \frac{ky'}{r'^2}, \frac{kz'}{r'^2}\right) = \zeta,$$

and the elements of length normal to the resulting surfaces $\xi, \eta, \zeta =$ constant are

$$dn'_\xi = d\xi/h'_\xi, \quad dn'_\eta = d\eta/h'_\eta, \quad dn'_\zeta = d\zeta/h'_\zeta,$$

with

$$\frac{1}{h'^2_\xi} = \left(\frac{\partial x'}{\partial \xi}\right)^2 + \left(\frac{\partial y'}{\partial \xi}\right)^2 + \left(\frac{\partial z'}{\partial \xi}\right)^2$$

and corresponding results for $\eta$ and $\zeta$, and Laplace's equation becomes

$$\frac{\partial}{\partial \xi}\left(\frac{h'_\xi}{h'_\eta h'_\zeta}\frac{\partial V'}{\partial \xi}\right) + \frac{\partial}{\partial \eta}\left(\frac{h'_\eta}{h'_\zeta h'_\xi}\frac{\partial V'}{\partial \eta}\right) + \frac{\partial}{\partial \zeta}\left(\frac{h'_\zeta}{h'_\xi h'_\eta}\frac{\partial V'}{\partial \zeta}\right) = 0. \quad (2)$$

Now we have

$$\frac{k^4}{h^2_\xi} = \Sigma\left[\frac{\partial}{\partial\xi}(k^2x)\right]^2 = \Sigma\left[\frac{\partial}{\partial\xi}(x'r^2)\right]^2,$$

$$= \Sigma\left(r^2\frac{\partial x'}{\partial\xi} + x'\frac{\partial r^2}{\partial\xi}\right)^2,$$

$$= \frac{r^4}{h'^2_\xi} + r'^2\left(\frac{\partial r^2}{\partial\xi}\right)^2 + r^2\frac{\partial r^2}{\partial\xi}\Sigma\, 2x'\frac{\partial x'}{\partial\xi},$$

$$= \frac{r^4}{h'^2_\xi} + r'^2\left(\frac{\partial r^2}{\partial\xi}\right)^2 + r^2\frac{\partial r^2}{\partial\xi}\cdot\frac{\partial r'^2}{\partial\xi},$$

$$= \frac{r^4}{h'^2_\xi} + \frac{\partial r^2}{\partial\xi}\cdot\frac{\partial}{\partial\xi}(r^2r'^2),$$

$$= \frac{r^4}{h'^2_\xi}$$

Hence

$$h'^2_\xi/h^2_\xi = h'^2_\eta/h^2_\eta = h'^2_\zeta/h^2_\zeta = k^2/r'^2 = r^2/k^2 = r/r'.$$

The equation for V′ may therefore be written

$$\frac{\partial}{\partial\xi}\left(\frac{h_\xi}{h_\eta h_\zeta}\cdot\frac{1}{r^2}\frac{\partial V}{\partial\xi}\right) + \frac{\partial}{\partial\eta}\left(\frac{h_\eta}{h_\zeta h_\xi}\cdot\frac{1}{r^2}\frac{\partial V'}{\partial\eta}\right) + \frac{\partial}{\partial\zeta}\left(\frac{h_\zeta}{h_\xi h_\eta}\cdot\frac{1}{r^2}\frac{\partial V'}{\partial\zeta}\right) = 0;$$

and in virtue of the relation

$$\frac{1}{r^2}\frac{\partial V'}{\partial\xi} = \frac{1}{r}\frac{\partial}{\partial\xi}\left(\frac{V'}{r}\right) - \frac{V'}{r}\frac{\partial}{\partial\xi}\left(\frac{1}{r}\right)$$

and corresponding relations for $\eta$ and $\zeta$, it becomes

$$\frac{\partial}{\partial\xi}\left(\frac{h_\xi}{h_\eta h_\zeta}\cdot\frac{1}{r}\frac{\partial}{\partial\xi}\left(\frac{V'}{r}\right)\right) + \ldots + \ldots - \frac{\partial}{\partial\xi}\left(\frac{h_\xi}{h_\eta h_\zeta}\cdot\frac{V'}{r}\frac{\partial}{\partial\xi}\left(\frac{1}{r}\right)\right) - \ldots - \ldots = 0$$

or

$$\frac{1}{r}\left\{\frac{\partial}{\partial\xi}\left(\frac{h_\xi}{h_\eta h_\zeta}\frac{\partial}{\partial\xi}\left(\frac{V'}{r}\right)\right) + \ldots + \ldots\right\} - \frac{V'}{r}\left\{\frac{\partial}{\partial\xi}\left(\frac{h_\xi}{h_\eta h_\zeta}\frac{\partial}{\partial\xi}\left(\frac{1}{r}\right)\right) + \ldots + \ldots\right\} = 0.$$

But $1/r$ is well known to be a solution of equation (1), and therefore it follows that $V'/r$ and V satisfy the same equation, namely the equation (1). If, then,

$$V' = f(\xi, \eta, \zeta)$$

is a solution of equation (2), we at once have a solution of equation (1) in the form

$$V = \frac{k}{r}V' = \frac{r'}{k}V' = \left(\frac{k}{r}, \frac{r'}{k}\right) f(\xi, \eta, \zeta).$$

It is of interest to exhibit the working of this theorem when the curvilinear coordinates $(\xi, \eta, \zeta)$ are the coordinates $(x, y, z)$ themselves. Taking harmonics of integral degree $n$ in $x, y, z$, we have, for example, when $n = -2$,

$$\frac{x}{r^3}, \quad \frac{y}{r^3}, \quad \frac{z}{r^3}, \quad \frac{z}{r^3}\tan^{-1}\frac{y}{x},$$

which yield

$$\frac{x}{r^2}, \frac{y}{r^2}, \frac{z}{r^2}, \frac{z}{r^2}\tan^{-1}\frac{y}{x} = k^2\{x', y', z', z'\tan^{-1}(y'/x')\},$$

harmonics for coordinates $(x', y', z')$ of order $n = 1$. Again, harmonics of order $n = -1$ in $(x, y, z)$ include

$$\frac{1}{r}, \frac{1}{r}\tan^{-1}\frac{y}{x}, \frac{1}{r}\log\frac{r+z}{r-z}, \frac{x}{x^2+y^2}, \frac{x}{r(r+z)},$$

which yield

$$1, \quad \tan^{-1}\frac{y}{x}, \quad \log\frac{r+z}{r-z}, \quad \frac{xr}{x^2+y^2}, \quad \frac{x}{r+z}$$

$$= 1, \quad \tan^{-1}\frac{y'}{x'}, \quad \log\frac{r'+z'}{r'-z'}, \quad \frac{x'r'}{x'^2+y'^2}, \quad \frac{x'}{r'+z'},$$

harmonics for coordinates $(x', y', z')$ of order $n = 0$. Corresponding sets of harmonics for $(x, y, z)$ of order $n$ and for $(x', y', z')$ of order $(-n-1)$ can be written down.

Again, suppose the radius vector $r$ is one of the curvilinear coordinates $(\xi, \eta, \zeta)$. Then we have solutions of equation (1) in the form

$$(Ar^n + Br^{-n-1})S,$$

where S is independent of $r$, which yield a solution

$$r(Ar^n + Br^{-n-1})S = (A'r'^{-n-1} + B'r'^n)S$$

of the equation (2). As a particular case, we may remark the fact that harmonics associated with a sphere $r = a$, namely

$$(Ar^n + Br^{-n-1})S_n,$$

where $S_n$ is a surface harmonic of degree $n$, yield the functions

$$(A'r'^{-n-1} + B'r'^n)S_n,$$

which are harmonics associated with the inverse surface, which is, of course, itself also a sphere.

When V and V′ are corresponding solutions of the equations (1) and (2), and stand in the relation

$$\frac{V}{V'} = \frac{r'}{k} = \frac{k}{r},$$

there is evidently a relation between the behaviour of V′ on the surface S′ and V on the surface S. Thus, suppose that on the surface S

$$V = \Sigma\Sigma\Sigma\, x^p y^q z^r / k^{p+q+r},$$

then on the surface S′

$$V' = \frac{k}{r'}\Sigma\Sigma\Sigma\, x'^p y'^q z'^r k^{p+q+r} / (r'^2)^{p+q+r}.$$

In particular, if on S

$$V = f_0 + g_0\left(\frac{k}{r}\right) + P_1(\cos\theta)\left\{f_1\left(\frac{r}{k}\right) + g_1\left(\frac{k}{r}\right)^2\right\} + P_2(\cos\theta)\left\{f_2\left(\frac{r}{k}\right)^2 + g_2\left(\frac{k}{r}\right)^3\right\} + \ldots,$$

then on S′

$$V' = f_0\frac{k}{r'} + g_0 + P_1(\cos\theta)\left\{f_1\left(\frac{k}{r'}\right) + g_1\left(\frac{r'}{k}\right)\right\} + P_2(\cos\theta)\left\{f_2\left(\frac{k}{r'}\right)^3 + g_2\left(\frac{r'}{k}\right)^2\right\} + \ldots.$$

Taking the simplest case of this result, we have $V = f_0$ on S. Then it follows that $V' = f_0 k/r'$ on S′. If, therefore, V is the potential when the conductor S is freely charged with electricity to potential $f_0$, then V′ is the potential thrown out by the conductor S′ when it is earthed in the presence of an electric charge $f_0 k$ at O′ the origin of coordinates and therefore the centre of inversion, so that

$$V' - f_0 k/r'$$

is the whole potential when the electric charge is disturbed by the presence of the conductor S earthed.

Further, if V is the potential thrown out by the conductor S when it is earthed in the presence of the external electric field whose potential is

$$V_0 = -f_n\left(\frac{r}{k}\right)^n P_n(\cos\theta),$$

so that on S

$$V + V_0 = 0,$$

then it follows that on S′

$$V' + V_0' = 0,$$

where

$$\frac{V}{V'} = \frac{V_0}{V_0'} = \frac{r'}{k} = \frac{k}{r},$$

so that V′ represents the potential thrown out by the conductor S′ when it is earthed in the presence of the external electric field whose potential is

$$V_0' = \frac{r}{k} V_0 = -f_n \left(\frac{r}{k}\right)^{n+1} P_n(\cos\theta) = -f_n \left(\frac{k}{r'}\right)^{n+1} P_n(\cos\theta).$$

The case when $n=1$ is of special interest. For if V is the potential thrown out by the conductor S when it is earthed in the presence of the uniform field whose potential is

$$V_0 = -\frac{f}{k} r\cos\theta,$$

then

$$V' = \left(\frac{r}{k}, \frac{k}{r'}\right) V$$

is the potential thrown out by the conductor S′ when it is earthed in the presence of the doublet at the centre of inversion, of strength $-fk^2$ whose potential is

$$V_0' = -fk^2 . \cos\theta / r'^2.$$

In these various electrostatic applications it is of interest to notice the simple relation between $\sigma$ the surface density on S (given by $\xi = \xi_0$) when the whole potential is V and $\sigma'$ the surface density on S′ (also given by $\xi = \xi_0$) when the whole potential is V′, and

$$\frac{V}{V'} = \frac{k}{r} = \frac{r'}{k},$$

both the conductors being earthed. Now

$$4\pi\sigma = -\left(h_\xi \frac{\partial V}{\partial \xi}\right)_{\xi=\xi_0} = -\left(\frac{r'^2}{k^2} h'_\xi \frac{\partial V}{\partial \xi}\right)_{\xi=\xi_0}$$

and

$$4\pi\sigma' = -\left(h'_\xi \frac{\partial V'}{\partial \xi}\right)_{\xi=\xi_0} = -\left(h'_\xi \frac{\partial}{\partial \xi}\left(\frac{rV}{k}\right)\right)_{\xi=\xi_0}$$

$$= -\left(\frac{r}{k} h_{\xi'} \frac{\partial V}{\partial \xi}\right)_{\xi=\xi_0}$$

since $V=0$ on the surface S. Therefore

$$\frac{\sigma}{\sigma'} = \frac{k^3}{r^3} = \frac{r'^3}{k^3} = \left(\frac{r}{r'}\right)^{-3/2}.$$

*Neumann's Transformation.*

The general theorem proved in this paper takes an interesting form when the surface S is a surface of revolution. For writing, as usual,

$$\rho^2 = x^2+y^2,$$
$$\rho'^2 = x'^2+y'^2.$$

V a solution of Laplace's equation in coordinates $(x, y, z)$ yields V′, a solution of Laplace's equation in coordinates $(x', y', z')$, such that

$$\frac{\mathrm{V}}{\mathrm{V}'} = \frac{r'}{k} = \frac{k}{r} = \left(\frac{\rho'}{\rho}\right)^{1/2}.$$

Thus, if subsidiary functions

$$\mathrm{W} = \mathrm{V}\rho^{1/2}, \quad \mathrm{W}' = \mathrm{V}'\rho'^{1/2}$$

are introduced, they satisfy the same equation. This fact is the basis of Neumann's transformation *, which has been much in vogue in the treatment of problems about surfaces of revolution. The use of W has, however, nothing to recommend it, and, in view of our general theorem, it is plainly more satisfactory to find a solution V and then deduce a solution V′ in the form

$$\mathrm{V}' = \frac{\mathrm{V}r}{k} = \frac{\mathrm{V}k}{r'}$$

rather than to introduce the subsidiary function W.

It will, of course, be the case that V and V′ may differ in important characteristics, as, for example, if

$$\mathrm{V} = f_1(\xi) f_2(\eta) f_3(\zeta)$$

with the variables separable. Then

$$\mathrm{V}' = \frac{k}{r'}\mathrm{V} = \frac{k}{r'} f_1(\xi) f_2(\eta) f_3(\zeta);$$

and since the variables are not in general separable in $r'$, V′ is not a solution in which the variables are separable.

This fact about V and V′ is evidently of importance in a methodological study † of various kinds of solutions of Laplace's equation which are of product type (in which the variables are separable) and of other related types.

* C. Neumann, 'Theorie der Electricitäts- und Wärme-Vertheilung in einem Ringe.' Halle, 1864; A. B. Basset, 'A Treatise on Hydrodynamics,' Cambridge, 1888, vol. ii. p. 8 *et seq.*

† Wrinch and Nicholson, Proc. Roy. Soc. June 1925.

*Stokes's Stream Function.*

It may be remarked that Stokes's Stream Function $\psi$, used in hydrodynamical problems in which there is symmetry about the axis of $z$, has a property similar to the property of the potential function V discussed above. For, if $(\xi, \eta, \zeta)$ be the curvilinear coordinates, $\zeta$ being the azimuthal angle, $\psi$ is defined by

$$\frac{h_\eta}{\rho}\frac{\partial \psi}{\partial \eta} = -h_\xi \frac{\partial V}{\partial \xi}, \quad \frac{h_\xi}{\rho}\frac{\partial \psi}{\partial \xi} = -h_\eta \frac{\partial V}{\partial \eta}.$$

Then $\psi$ satisfies the equation

$$\frac{\partial}{\partial \xi}\left(\frac{h_\xi}{h_\eta \rho}\frac{\partial \psi}{\partial \xi}\right) + \frac{\partial}{\partial \eta}\left(\frac{h_\eta}{h_\xi \rho}\frac{\partial \psi}{\partial \eta}\right) = 0. \quad . \quad . \quad . \quad (3)$$

The stream function $\psi'$ for the coordinates $(z', \rho')$ inverse to the coordinates $(z, \rho)$ satisfies the equation

$$\frac{\partial}{\partial \xi}\left(\frac{h'_\xi}{h'_\eta \rho'}\frac{\partial \psi'}{\partial \xi}\right) + \frac{\partial}{\partial \eta}\left(\frac{h'_\eta}{h'_\xi \rho'}\frac{\partial \psi'}{\partial \eta}\right) = 0. \quad . \quad . \quad (4)$$

In virtue of the relations between $z$, $\rho$, $h_\xi$, $h_\eta$ and $z'$, $\rho'$, $h'_\xi$, $h'_\eta$, namely

$$\frac{z}{z'} = \frac{\rho}{\rho'} = \frac{r}{r'} = \frac{h'_\xi}{h_\xi} = \frac{h'_\eta}{h_\eta} = \frac{k^2}{r'^2} = \frac{r^2}{k^2},$$

the equation for $\psi'$ becomes

$$\frac{\partial}{\partial \xi}\left(\frac{h_\xi}{h_\eta \rho} \cdot r^2 \frac{\partial \psi'}{\partial \xi}\right) + \frac{\partial}{\partial \eta}\left(\frac{h_\eta}{h_\xi \rho} \cdot r^2 \frac{\partial \psi'}{\partial \xi}\right) = 0.$$

Since

$$r^2 \frac{\partial \psi'}{\partial \xi} = r\frac{\partial}{\partial \xi}(r\psi') - r\psi'\frac{\partial r}{\partial \xi}$$

with a similar result for $\eta$, it further changes to

$$\frac{\partial}{\partial \xi}\left(\frac{h_\xi}{h_\eta \rho} \cdot r \frac{\partial}{\partial \xi}(r\psi')\right) + \frac{\partial}{\partial \eta}\left(\frac{h_\eta}{h_\xi \rho} \cdot r \frac{\partial}{\partial \eta}(r\psi')\right)$$
$$- \frac{\partial}{\partial \xi}\left(\frac{h_\xi}{h_\eta \rho} \cdot r\psi' \frac{\partial r}{\partial \xi}\right) - \frac{\partial}{\partial \eta}\left(\frac{h_\eta}{h_\xi \rho} \cdot r\psi' \frac{\partial r}{\partial \eta}\right) = 0$$

or

$$r\left\{\frac{\partial}{\partial \xi}\left(\frac{h_\xi}{h_\eta \rho}\frac{\partial}{\partial \xi}(r\psi')\right) + \frac{\partial}{\partial \eta}\left(\frac{h_\eta}{h_\xi \rho}\frac{\partial}{\partial \eta}(r\psi')\right)\right\}$$
$$- r\psi'\left\{\frac{\partial}{\partial \xi}\left(\frac{h_\xi}{h_\eta \rho}\frac{\partial r}{\partial \xi}\right) + \frac{\partial}{\partial \eta}\left(\frac{h_\eta}{h_\xi \rho}\frac{\partial r}{\partial \eta}\right)\right\} = 0.$$

But, $r$ is a solution of the equation for $\psi$, and therefore $r\psi'$ and $\psi$ satisfy the same equation. This result enables us to derive, from a solution $\psi$ of equation (3) a solution

$$\psi' = \frac{k}{r}\psi = \frac{r'}{k}\psi$$

of equation (4). Thus, for example *, in the case of the ovary spheroids given by $\eta =$ constant in the transformation

$$z' + i\rho' = c' \cos(\xi - i\eta)$$

we have

$$\psi' = \rho' \sum_1^\infty P_n^1(\cos\xi)\{A_n P_n^1(\cosh\eta) + B_n P_n^1(\cosh\eta)\},$$

and the solutions appropriate (*e. g.*) for motion outside a specific spheroid will have $B_n = 0$. Then we have at once a general solution,

$$\begin{aligned}\psi &= \left(\frac{r}{k}, \frac{k}{r'}\right)\psi', \\ &= \frac{k\rho'}{r'} \sum_1^\infty P_n^1(\cos\xi)\{A_n Q_n^1(\cosh\eta) + B_n P_n^1(\cosh\eta)\}, \\ &= \frac{k\rho}{r} \sum_1^\infty P_n^1(\cos\xi)\{A_n Q_n^1 \cosh\eta) + B_n P_n^1(\cosh\eta)\},\end{aligned}$$

appropriate in the case of the inverted ovary spheroids given by $\eta =$ constant in the transformation

$$z + i\rho = c \sec(\xi + i\eta),$$

and when the motion is outside a specific surface belonging to this class, $A_n = 0$.

---

CXIV. *Viscous Flow through Wide-Angled Cones.* By W. N. Bond, *B.A., D.Sc., F.Inst.P., Lecturer in Physics, University College, Reading* †.

*Summary.*

Experiments are described on the flow of liquid with negligible kinetic energy through cones of very large angle, where peculiar results are to be expected owing to the velocity-gradient in the direction of motion and the corresponding forces due to viscosity.

With converging flow through cones of semi-angle not greater than 90°, the velocities and reversal of radial pressure-gradient agree with the theory. For larger angles of cone a reversal of velocity is found, but not in the way predicted by the theory. One of the postulates is not satisfied, and the theory is therefore not applicable.

---

* Basset, *loc. cit.* p. 12 *et seq.*

† Communicated by the Author.

## *Introduction.*

THE experiments described in this paper were undertaken to test the application of the hydrodynamical equations to fluid of constant density flowing with negligible kinetic energy through wide-angled cones of circular cross-section. It is assumed in the calculations that the flow takes place along straight stream-lines passing through the apex of the cone. The theory, which has been given by W. J. Harrison *, will first be considered. Its rather peculiar predictions are due to the viscosity effects contributed by the variation in velocity *in the direction of motion*, and would not occur if the only frictional forces called into play were due to the velocity-gradients normal to the direction of motion.

Choosing the apex of the cone for the origin of polar coordinates, the velocity $u$, measured *outwards* from the apex, may be written

$$u=f(\theta)/r^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The hydrodynamical equations, in which the terms depending on kinetic energy have been neglected, then take the form

$$f'''(\theta)+f''(\theta)\,.\,\cot\theta+f'(\theta)\,.\,(6-\operatorname{cosec}^2\theta)=0. \quad . \quad (2)$$

In the present case $\left(\frac{\partial u}{\partial\theta}\right)_{\theta=0}=0$ and $(u)_{\theta=\alpha}=0$, where $\alpha$ is the semi-angle of the cone of fluid. The solution of equation (2) then becomes

$$f(\theta)=\mathrm{C}(\cos 2\theta-\cos 2\alpha). \quad . \quad . \quad . \quad . \quad (3)$$

If the volume per second of fluid passing radially *outwards* through the cone be denoted by Q, equations 1 and 3 give

$$u=\frac{3(\cos 2\theta-\cos 2\alpha)}{4\pi(2\cos^3\alpha-3\cos^2\alpha+1)}\cdot\frac{\mathrm{Q}}{r^2}. \quad . \quad . \quad (4)$$

Since $u\propto(\cos 2\theta-\cos 2\alpha)$, the velocity becomes zero when $\theta=\pi-\alpha$; and for larger values of $\theta$ the flow is reversed in sense. This predicted reversal in sense is one of the subjects investigated in this paper.

For small values of $\theta$, $(\cos 2\theta-\cos 2\alpha)$ is not negative; and $(2\cos^3\alpha-3\cos^2\alpha+1)$ is positive for $\alpha<\frac{2\pi}{3}$. Under these conditions, $u$ for small values of $\theta$ has the same sign as Q. [But when $\alpha>\frac{2\pi}{3}$, if the velocity for small values of $\theta$ is negative, or towards the apex of the cone, the net volume of fluid passing per second is positive, or outwards.]

* Proc. Camb. Phil. Soc. vol. xix. pp. 311–12.

Returning to the calculation, it follows that the pressure gradients (after deducting that due to difference in level) are given by

$$\frac{\partial p}{\partial \theta} = -\frac{3}{\pi} \cdot \frac{\sin 2\theta}{2\cos^3 \alpha - 3\cos^2 \alpha + 1} \cdot \frac{\mu Q}{r^3}, \quad . \quad . \quad (5)$$

$$\frac{\partial p}{\partial r} = -\frac{3}{\pi} \cdot \frac{2 - 3\sin^2 \theta}{2\cos^3 \alpha - 3\cos^2 \alpha + 1} \cdot \frac{\mu Q}{r^4}, \quad . \quad . \quad (6)$$

where $\mu$ denotes the viscosity of the fluid.

The value of $\frac{\partial p}{\partial r}$ is zero when $\sin^2\theta = \frac{2}{3}$ or $\theta = 54^\circ\ 45'$. When the velocity for small values of $\theta$ is negative (towards the cone apex), the pressure gradient $\frac{\partial p}{\partial r}$ is positive for small values of $\theta$; but for values of $\theta$ greater than $54^\circ\ 45'$ the radial pressure gradient is reversed in sense. This reversal is investigated in the present experiments.

*General Scope of the Experiments.*

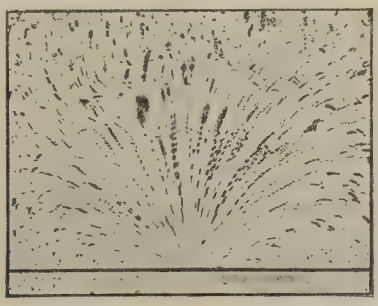
It results from the theory given above that for cones of large semi-angle the pressure gradient $\frac{\partial p}{\partial r}$ might be expected to be reversed in sense at angles $\theta > 54^\circ\ 45'$. And further, if $\alpha > \frac{\pi}{2}$, the velocity might be reversed in sense at angles $\theta > (\pi - \alpha)$. These predictions are based on the assumptions of symmetry about the axis of the cone, stream-line flow in straight lines directed towards the apex of the cone, negligible kinetic energy, and the truth of the usual hydrodynamical equations. It will be seen later that when the predictions are not verified, the second of the above assumptions is not true.

In order to test these predictions, observations may be made of velocity at chosen points, or of pressure difference between points on the boundaries, wide-angled cones being used. For the kinetic energy of the fluid to be negligible, $Q\rho/r\mu$ must be small (where $\rho$ denotes the density of the fluid). Since it is desirable that $Q/r^2$ and $Q\mu/r^4$ should not be too small, $\mu$ was made large and Q and $r$ small in the present experiments. The flow was arranged towards the cone apex (Q negative) in order to reduce any possible tendency to turbulence.

*Measurements of Velocity.*

For these experiments a tank was used (9 cm. cube), having two of its sides glass, its base being either plane or formed by a cone, of which the apex projected into the tank. In this way liquid cones of semi-angles $\alpha = 90°$, 110°, 141°, and 160° were obtained. Some glycerine (containing a small amount of water) was shaken to introduce air-bubbles and, after the larger bubbles had risen, was poured into the tank. It then flowed by gravitation through a hole drilled along the axis of the cone, or in the plane base. A parallel beam of light from an arc-lamp was reflected vertically downwards on to the top of the liquid, where it passed through a straight slit, so as to illuminate the air-bubbles lying in a vertical plane passing through the hole or "sink" and parallel to the glass sides of the tank. A photograph was then taken of the bubbles as viewed through a side of the tank. By exposing and screening the photographic plate alternately for equal known intervals of time, each bubble was made to yield a series of dashes (figs. 1 and 3) on the photographic plate. The camera magnification having been found, the velocities for various values of $r$ and $\theta$ could be determined from the photograph.

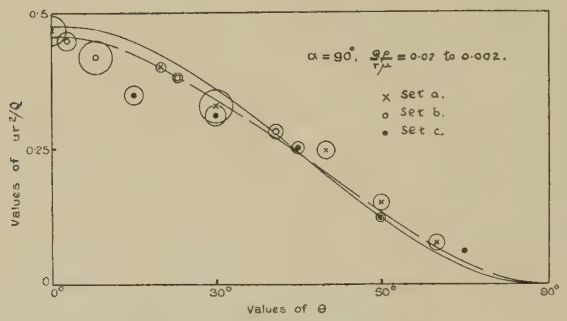
Fig. 1.



When $\alpha = 90°$ (fig. 1) the stream-lines were almost straight ($u \propto 1/r^2$), except near to the hole or "sink." Experimental values of $ur^2/Q$ are plotted against $\theta$ in fig. 2, each point representing the average of several measurements, the root-mean-square error of the average being indicated. The value of $Q\rho/r\mu$ varied between about 0·02 and 0·002. The dotted curve has been drawn to represent the observations and satisfy the conditions $\left(\frac{\partial u}{\partial \theta}\right)_{\theta=0} = 0$ and $(u)_{\theta=\alpha} = 0$. The continuous curve represents equation (4). It will be seen

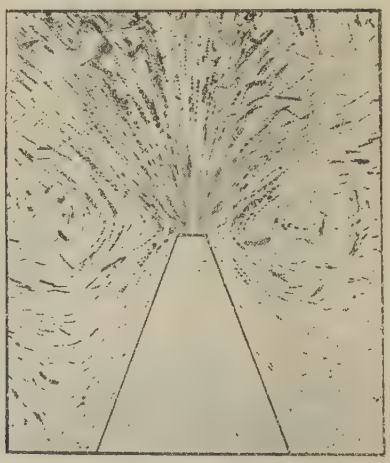
that the experimental curve passes within less than the root-mean-square error of 11 of the 14 points for which error is known, and differs little from the curve predicted by equation (4).

Fig. 2.




When liquid cones having semi-angles $\alpha = 110°$, 141°, and 160° were used, the liquid near the axis moved in almost straight lines towards the hole at the apex of the solid cone (fig. 3). But the fluid originally at angles greater than about $\theta = 72°$, 43°, and 37° respectively, and less than $\theta = 90°$,

Fig. 3.



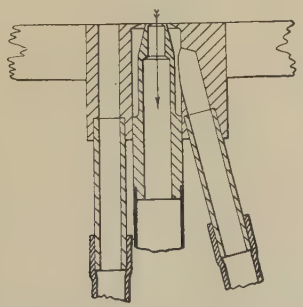
did not pass through the tube out of the tank, but after approaching the apex of the cone receded at angles $\theta$ given by $90° < \theta < \alpha$. Thus a slowly moving ring-eddy existed, whose axis coincided with that of the cone. This eddy appears in section at either side of fig. 3. The eddy does not agree with the predictions given in the first part of this

paper. On inspection of fig. 3 it will be found that near the centre of the eddy the stream-lines do not approximate to straight lines directed towards the cone apex, even at points distant from the "sink" and the tank-walls. Hence the above theory cannot be used, as one of the postulates is not satisfied.

*Pressure-Difference Experiments.*

In order to test whether the radial pressure-difference is reversed in sense for points at angles $\theta > 54° 45'$, a flat plate (or cone of semi-angle $\alpha = 90°$) was used, the difference in pressure being measured between two holes in the walls at different distances from the centre. An inward flow (Q negative) was used as before. Since the radial pressure-gradient varies as $1/r^4$, one of the two pressure-holes must be near to the central hole or "sink" for the pressure-difference to be large enough to be measurable. The exact position of the second, more distant, pressure-hole matters little. The inner pressure-hole must not be so near the central hole that the local curvature of the stream-lines causes error. It is evident, however, that this error fortunately diminishes rapidly with distance from the centre.

Fig. 4.

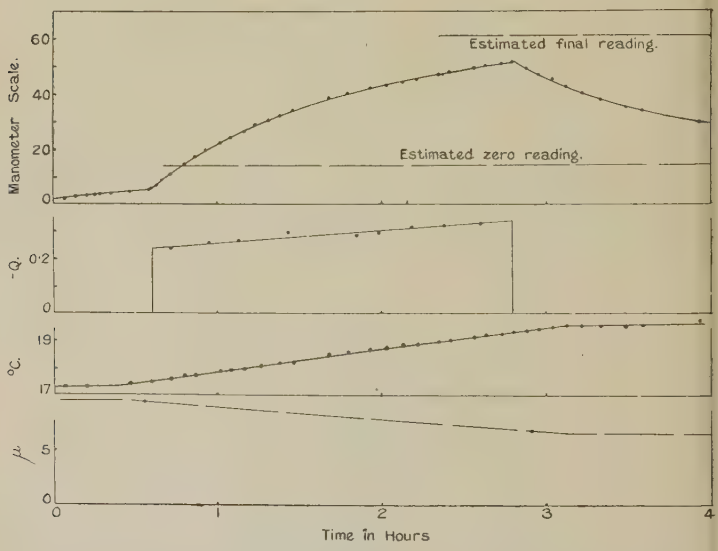


Owing to the large viscosity of the liquid used, any "U" tube, or similar manometer, connected to the two pressure-holes, will be very slow in attaining a reading. On account of surface tension, it is not desirable to make the "U" tube limbs narrow, and by this means to reduce the volume of liquid that must pass into and out of the manometer for it to reach its final reading. Any increase in the rate of movement of the manometer must be made by enlarging the two pressure-holes and the connecting tubes. The outer pressure-hole was therefore made large, and the inner one made in the form of a circular slot concentric with the central hole (fig. 4). The slot had thus a large area without

causing undue disturbance to the liquid flow in the tank, and without the distances of the inner and outer edges of the slot from the central hole differing much.

The pressure-difference was measured with a " U " tube (limb diameter 2·5 c.m.), containing a mixture of petrol and carbon tetrachloride of approximate density $\rho' = 1{\cdot}40$. The glycerine in the tank and the upper part of the " U " tube had a density of about $\rho = 1{\cdot}25$. The position of the meniscus was read by means of a microscope fitted with an eyepiece scale, on which a displacement of 0·001 cm. could be detected.

Fig. 5.




In the preliminary experiments it was found that the meniscus in the limb connected to the outer pressure-hole began rising when flow was started, then fell whilst flow was stopped, and commenced rising again when flow was restarted. Thus (for Q negative) the pressure when flow took place was larger at the inner than at the outer pressure-hole, as predicted by the theory. Experiments were then performed, the values of Q and $\mu$ being measured, and the manometer reading continued long enough to obtain an exponential curve showing its mode of approach to its final position. From these curves (one of which is given in fig. 5), the final reading of the manometer was estimated.

Two different positions of the inner pressure-slot were

used, and in most of the experiments a constant difference of level was maintained automatically between the liquid surface in the tank and that at the exit from the system.

When $\alpha=90°$ and $\theta=90°$, equation (6) takes the form

$$\frac{\partial p}{\partial r}=\frac{3}{\pi}\cdot\frac{\mu Q}{r^4}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and the excess of the pressure at the inner pressure-slot over that at the outer pressure-hole is given by

$$p_1-p_2=-\frac{1}{\pi}\mu Q\left(\frac{1}{r_1^3}-\frac{1}{r_2^3}\right), \quad . \quad . \quad . \quad . \quad (8)$$

where suffixes 1 and 2 denote the inner and outer pressure-holes respectively. The term depending on $r_2$ was small, and this equation could be used to deduce from the measurements of $r_2$, $p_1-p_2$, $\mu$, and Q the effective value of the distance from the centre of the system to the inner pressure-slot ($r_1$). The values thus found are given in the following Table, together with the radii of the inner and outer edges of the pressure-slot as obtained by direct measurement :—

$\alpha=90°$; $\theta=90°$; $r_2=0$ 89 cm. (hole radius 0·2 cm.); radius of central hole, 0·088 cm.

| Q (mean). | $\mu$ (mean). | $p_1-p_2$. | $\frac{\pi(p_1-p_2)}{-Q\mu}$. | Effective $r_1$ (deduced). | $r_1$ (direct measurement). mean. | max. | min. | $\frac{Q}{r}\frac{\rho}{\mu}$ (max.). |
|---|---|---|---|---|---|---|---|---|
| −0·11 | 9·4 | 32·0 | 97·1 | $0·21_8$ | | | | 0·07 |
| −0·13 | 8·4 | 26·5 | 76·3 | $0·23_4$ | $0·21_8$ | $0·24_4$ | $0·19_2$ | 0·10 |
| $-0·28_5$ | 7·9 | 58·9 | 81·9 | $0·23_0$ | | | | 0·24 |
| −1·16 | 5·4 | 55·2 | 28·6 | $0·32_2$ | $0·29_2$ | $0·31_2$ | $0·27_1$ | 0·85 |

In all the experiments the pressure was found greater at the inner than at the outer pressure-hole (for Q negative, or flow inwards towards the apex of the cone); and the pressure-difference varied in the way expected when the value of $r_1$ was changed. For the two values of $r_1$ used, the observed values of $(p_1-p_2)$ were respectively 12 and 28 per cent. less than the predicted, the deduced effective values of $r_1$ being 4 and 9 per cent. larger than was to be expected. Thus, for the first apparatus, the effective position of the pressure-slot was estimated to be further out than its central line by an amount equal to a sixth of the width of the slot; and, for the second apparatus, to be further out than the outer edge of the slot by a quarter of its width.

These errors might be due to the difficulty of measuring a pressure-difference so small as 40 dynes/cm.$^2$, when the manometer takes half an hour or more to move half-way towards its reading. Even with the large diameter of manometer tubes used (2·5 cm.), variable surface tension effects might possibly account for an error in the direction found, of about the observed magnitude. Any increase in the diameter of these tubes would have caused the manometer to move yet more slowly towards its reading, and was hence inadvisable. The effect of neglecting the kinetic energy of the liquid would cause an error in the direction observed. But it can be shown that the error would be small provided $Q\rho/r\mu$ were small compared with about 20; and in the present experiments $Q\rho/r\mu$ never exceeded 0·85, and was on the average considerably less than this. Other possible causes of error are the difficulty of predicting how nearly the mean radius of the pressure-slot can be assumed to represent its effective radius; the local curvature of the stream-lines near the central hole or "sink"; and the fact that in fig. 1 the stream-lines are not quite straight even at a distance from the "sink."

Summarising, it is found that (for Q negative) the theoretical predictions are verified when $\alpha$ is not greater than 90°, though the agreement is not quite perfect. For angles $\alpha > 90°$, one of the postulates is found not to be satisfied, the flow observed being depicted in fig. 3.

The Author would like to thank Prof. J. A. Crowther for the facilities that have made these experiments possible and for his kind encouragement throughout the work; Mr. R. C. Walker for making some of the preliminary attempts at the experiments; and Mr. J. S. Burgess, the laboratory steward, for continued help in the construction of the apparatus.

University College,
Reading,
June 10, 1925.

---

CXV. *Some Electrode Phenomena in Electrolysis.* *By* J. A. Crowther, *M.A., Sc.D., F.Inst.P., Professor of Physics in University College, Reading, and* R. J. Stephenson, *B.Sc.**

IN a previous communication (Phil. Mag. xlix. p. 86, July 1925) it was shown by the authors that if a gradually increasing potential difference is applied to an electrolytic cell, one of the electrodes of which was of comparatively small area, the current at first increased linearly with the

* Communicated by the Authors.

applied electromotive force. When a certain current density was reached, however, the current ceased to increase with increasing P.D. and, after passing through a stage where both current and voltage fluctuated largely, became steady again at a very much smaller value. After this point the current decreased steadily as the applied P.D. was increased. In one series of experiments, for example, the current increased uniformly up to 16 amperes, which was reached with a P.D. of 12 volts, then became irregular, until the P.D. reached 60 volts, when the corresponding current was 0·7 ampere, which was further reduced to 0·2 ampere when the P.D. was increased to 200 volts. For a given electrolyte the critical current was directly proportional to the area of the small electrode, that is to say the effect depended on the current density at the electrode. It was found to be independent of the shape and material of the electrode (providing the electrode was not appreciably attacked by the electrolyte), but varied with the nature and strength of the electrolytic solution. The phenomenon was shown, in the paper referred to, to explain the action of the electrolytic interrupter. It seemed, however, to be sufficiently intriguing to be worth further study on its own account.

It was found that the change in resistance of the cell was invariably attended by a characteristic change in the mode of evolution of the gas at the small electrode. Instead of the normal emission of small bubbles from the whole of the electrode, when the cell was in the highly resistant condition the electrode appeared as if it were enclosed in an elastic skin, between which and the electrode itself the gases evolved forced their way upwards to be emitted from the top of the electrode in a slow succession of large bubbles. If the appearance is genuine and if there is a continuous gas film between the electrolyte and the electrode, this would in itself be sufficient to account for the large resistance of the cell. It would still, however, be necessary to account for the formation of the film.

To investigate matters further a search point, consisting of a fine platinum wire sealed into a glass sheath so that only its tip projected from the glass, was introduced into the cell. It was mounted on the carrier of a travelling microscope so that the distance between the point and the electrode could be gradually varied. The search point was connected to the electrode through a high resistance voltmeter. The electrode used was a flat platinum disk 0·5 sq. cm. in area, and the electrolyte was dilute sulphuric acid of S.G. 1·20. The cell was thrown into the highly resistant stage by

applying a P.D. of 100 volts between the electrodes, and the current through the cell was then $\frac{1}{2}$ ampere. The resistance of the cell in its normal state was about 1 ohm.

The P.D. between the search point and the electrode was initially 96 volts, and remained practically constant at this value as the distance from the electrode was gradually reduced until the search point was almost in contact with the electrode. Just before contact was established it fell instantaneously to zero. It was not found possible to measure with any accuracy the distance between the search point and the electrode at which this sudden fall occurred, but it was certainly less than 1/50 mm. One of the difficulties which prevented accurate measurement was that the electrostatic field between the two was so great (about 50,000 volts per cm.) that fragments of platinum were torn from the electrode and bridged the gap. The extra resistance is thus confined to a layer which certainly does not extend to more than 1/50 mm. from the electrode.

It may be mentioned in passing that it was thought possible that the current in the resistant stage might be held up, not by resistance, but by a back E.M.F., due perhaps to an accumulation of undischarged ions at the small electrode. The experiment was therefore made of working the cell, when in this stage, in a calorimeter, and determining from the heat produced the dissipation of electrical energy in the cell. This was found to be, within one or two per cent., what was to be expected if the cell were acting as a pure resistance. The layer acts, therefore, as a resistance and not as an E.M.F.

Experiments were then made to determine the critical conditions for a series of solutions of the same electrolyte, but of different strengths and hence of different conductivities. The conductivities of these solutions were compared by the Kohlrausch bridge. The electrolytic cell used in these experiments consisted of a platinum wire projecting through a glass sheath into the electrolyte, which was used as the anode; the cathode was a large sheet of lead. The exposed area of the small platinum electrode was 0·4 sq. cm. As is well known to users of the Wehnelt electrolytic break, the platinum wire, if used as the cathode, invariably fuses at large current densities. We have, however, found that it is possible to reproduce all the phenomena described with the small electrode as the cathode, if the latter takes the form of a plate instead of a wire and if adequate means are employed to remove the heat generated. Using an electrode consisting of a lead rod faced with platinum, the end being

flush with a protecting sheath of glass, the phenomena were the same, and occurred at approximately the same critical conditions, whether the electrode was positive or negative. In practice, however, it is difficult to prevent the electrolyte from attacking the lead support, and a wire electrode was usually employed and made the anode.

A set of observations made with sulphuric acid as the electrolyte are reproduced in Table I. The first column

TABLE I.

Sulphuric acid. Area of platinum anode 0·4 sq. cm.

| Relative specific resistance. | Critical voltage. | Critical current. | Current for P.D. of 98 volts. |
|---|---|---|---|
| | volts. | amps. | amps. |
| 1·00 | 12 | 17 | 1·0 |
| 1·23 | 14 | 15 | 1·2 |
| 1·23 * | 14 | 16 | 0·9 |
| 1·69 | 15 | 13·3 | 1·2 |
| 2·50 | 16 | 12 | 1·5 |
| 3·45 | 21 | 10·4 | 1·6 |
| 4·10 | 24 | 10 | 1·8 |

* Solution of strength greater than max. conductivity.

gives the relative specific resistance of the solution, that of the most conducting being taken as unity. The second column gives the P.D. across the cell at which the latter passed over to the highly resistant state, and the third the corresponding current. The readings for the P.D. were taken with a high resistance voltmeter connected across the electrodes. It will be seen that neither the critical voltage nor the critical current is constant. The critical voltage at which the cell passes into the highly resistant state increases with increase in specific resistance ; the critical current diminishes. This observation is found to apply to all the electrolytes investigated.

It is, however, hardly to be expected that the formation of the resistant layer will depend directly on the applied P.D. across the cell. A portion of this P.D. is used up in driving the current through the bulk of the electrolyte, the energy expended being used in heating the liquid, and it is found experimentally that the temperature of the liquid as a

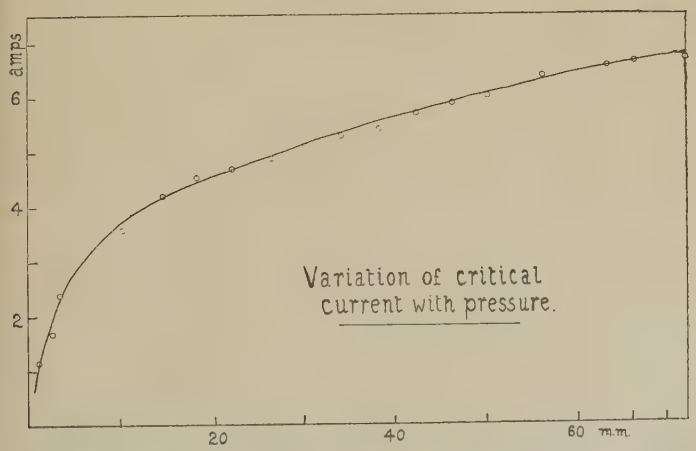
who e has curiously little effect on the phenomenon. Attempts were therefore made to estimate what proportion of the full voltage was used in this way. If the critical voltages from the second column of Table I. are plotted against the corresponding specific resistances the points are found to lie very nearly on a straight line, which if produced cuts the axis at a distance of 8 volts from the origin. If this extrapolation is legitimate, it would indicate that if the electrolytic resistance of the cell could be reduced to zero it would still require 8 volts to throw the cell into the resistant state. Of these 8 volts, 3 volts are accounted for by the polarization E.M.F. of the cell, leaving a balance of 5 volts to be explained. The most obvious explanation is that there is a resistance at the interface between the electrolyte and the electrode. Such a resistance has frequently been postulated under the name of "Transfer resistance," and a c nsiderable amount of evidence of a rather conflicting kind has been accumulated on the question.

To investigate the matter further the test point already described was again employed, but this time with the cell in it normal conducting state. This was again connected to the small electrode through a high resistance voltmeter. To determine when the test point was actually in contact with the electrode they were also joined by a subsidiary circuit containing a single Daniell cell and an electric bell. This circuit was broken when not required. When a constant current, less than the critical current, was passed through the cell and the point was gradually brought nearer the electrode, the P.D. between them steadily decreased until the moment when contact was about to be established. At this point it still had an appreciable value ; 4 volts in the case of sulphuric acid of S.G. 1·19, and 10 volts for acid of S.G. 1·020. If, however, the micrometer screw was turned very slightly so as to bring the point and electrode into actual contact, there was a sudden drop in the P.D. from 4 volts to 0·6 volt for the stronger acid and from 10 volts to 0·8 for the weaker. Intermediate voltages could not be obtained however carefully the screw was manipulated. These experiments again seem to indicate the existence of a transfer resistance at the surface of the electrode, a resistance which increases with the specific resistance of the electrolyte employed.

Evidence of a much stronger character is, however, supplied by experiments now to be described. It was thought that if the resistant layer was in reality gaseous, it might become larger and therefore more easily visible if the

pressure was reduced. An electrolytic cell with the usual platinum wire anode was constructed so that it could be made air-tight and evacuated to any desired pressure by a small pump. A vessel of several litres capacity was interposed between the cell and the pump to steady the pressure, which was read by a mercury vacuum gauge. At pressures of 1 or 2 cm. of mercury the separation between the electrode and the electrolyte was quite unmistakable. There was, in fact, quite a clear conical space, broadening upwards, surrounding the wire electrode. Other and more important phenomena were noticed. It was found that the critical current necessary to throw the cell into the resistant state was very much smaller at low pressures than at normal atmospheric pressure. In fact, at a pressure of 1 cm. of mercury it was impossible to pass a current of more than 1 ampere through the cell at any applied voltage. The relation between the pressure and the critical current for this particular cell is given in fig. 1.

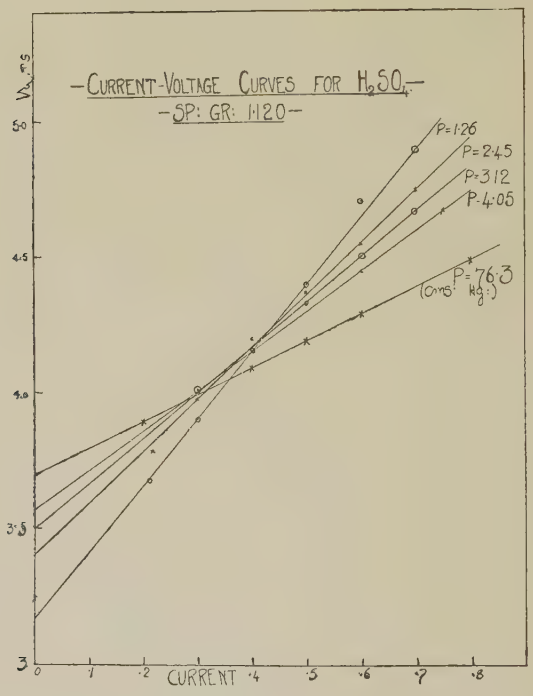
Fig. 1.




It was also observed that the resistance of the cell was apparently considerably greater at lower pressures. Accordingly a voltmeter was connected in parallel with the cell and the ammeter in series with it, and a set of current-voltage curves was taken for the cell at different pressures. A typical set of such curves is reproduced in fig. 2. These curves refer to the cell when in its normal conducting state. The particular set reproduced are for sulphuric acid of S.G. 1·12, but exactly similar sets were obtained with other electrolytes.

It will be seen that each curve is, as might be expected, a straight line cutting the axis of voltage at a point which represents the back E.M.F. of the cell. The slope of the line represents the ohmic resistance of the cell. It is clear from the diagram that, although nothing is changed in the

Fig. 2.




cell except the pressure, this resistance is not the same for all the curves, but increases steadily as the pressure is reduced. The values of the resistance of the cell at different pressures, as deduced from these curves, are given in Table II. for solutions of three different strengths.

The resistances, as thus measured, were then plotted against the reciprocals of the corresponding pressures, and the points so obtained were found to lie fairly accurately on a straight line, which cut the axis of resistance at some distance from the origin. Three such curves, for solutions of sulphuric acid of different densities, are reproduced in fig. 3. Exactly similar curves were obtained for solutions

TABLE II.

Variation of resistance with pressure.

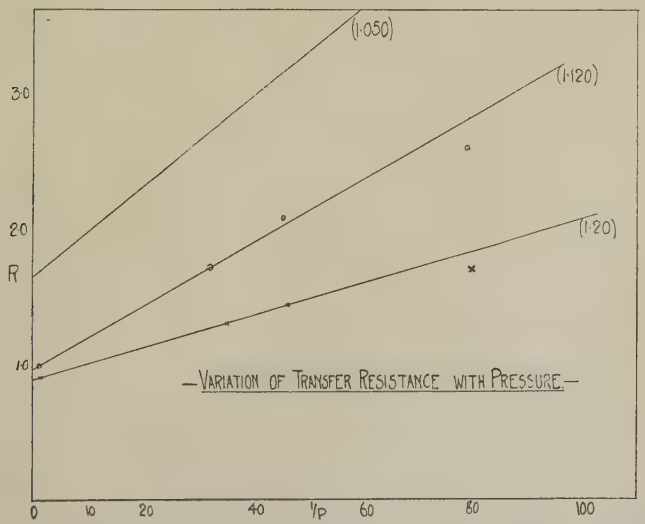
| Sulphuric Acid. | | | | | |
|---|---|---|---|---|---|
| S.G.=1·050. | | S.G.=1·120. | | S.G.=1·210. | |
| Pressure cm. of mercury. | Resistance ohms. | Pressure. | Resistance. | Pressure. | Resistance. |
| 76·3 | 1·68 | 76·3 | 0·98 | 76·3 | 0·90 |
| 3·92 | 2·5 | 4·05 | 1·48 | 3·60 | 1·14 |
| 3·06 | 2·8 | 3·12 | 1·70 | 2·87 | 1·29 |
| 2·36 | 3·02 | 2·45 | 1·94 | 2·15 | 1·42 |
| 1·45 | 3·6 | 1·26 | 2·5 | 1·26 | 1·61 |

of other electrolytes. For experiments conducted in this way the resistance of an electrolytic cell can be represented by an equation of the form

$$R = R_0 + \frac{k}{p},$$

where $p$ is the pressure in the cell, and $R_0$ and $k$ are constants for the same cell and the same solution.

Fig. 3.




It will further be seen from fig. 3 that for a given electrolyte the value of $k$ increases as the specific resistance of the

Table III.

Solutions of sulphuric acid of different strengths. Variation of transfer resistance with specific resistance of solution.

| Relative specific resistance $\sigma$. | $k$. | $k/\sigma \times 10^2$. |
|---|---|---|
| 1·00 | ·0152 | 1·52 |
| 1·50 | ·0235 | 1·56 |
| 1·68 | ·0242 | 1·44 |
| 2·20 | ·0314 | 1·17 |
| 3·04 | ·0335 | 1·10 |
| 5·90 | 041 | 0 70 |

solution is increased. The value of $k$ is, in fact, very nearly proportional to the specific resistance of the solution, but increases rather less rapidly at greater dilutions. This is shown by the figures for sulphuric acid in Table III. This proportionality does not hold as between solutions of different electrolytes. The value of $k$ for a solution of sodium chloride in water was distinctly greater than for a solution of sulphuric acid of the same specific conductivity.

It does not seem credible that the specific resistance of an electrolyte should depend appreciably on the pressure upon it; in fact, direct experiments in which the resistance of the solution was measured by a Kohlrausch bridge in the usual way gave no indication of any change in resistance with pressure over the range of pressures available. The constant part $R_0$ of the equation thus represents the true electrolytic resistance of the cell; the variable portion $k/p$ represents a transfer resistance which varies inversely as the pressure. It will be seen from the curves that while this transfer resistance is a small fraction of the whole resistance at atmospheric pressure, its existence is quite unmistakable when the cell is evacuated to a pressure of 1 or 2 cms. of mercury.

The relation between the transfer resistance and the pressure strongly suggests that this resistance is provided by a thin film of gas adhering to the surface of the electrode. The electrolytic ions, in order to reach the electrode, will have to pass through this gaseous layer, presumably in the form of gaseous ions. The mobility of a gaseous ion is inversely proportional to the pressure, but on the other hand the number of ions per unit volume in the gas will, for

the same current, be inversely proportional to the mobility, so that the specific resistance will be independent of the pressure in the layer. The thickness of the layer, however, assuming that Boyle's law is applicable within the layer, will be inversely proportional to the pressure. The resistance of the layer should thus be inversely proportional to the pressure, as is found to be the case.

The gas-film which causes the transfer resistance on this hypothesis is formed by the gas liberated on the electrode by the current, and a definite quantity of electricity must pass through the cell before the transfer resistance reaches its final value. This can readily be verified by including an oscillograph in the circuit. The resulting oscillograms show that when the current is made it rises instantaneously to a value considerably higher than its final steady value, to which it falls in a time which depends on the current density at the electrode, but is of the order $\frac{1}{100}$ sec. for the currents employed in these experiments. The difference between the initial and the final current becomes more marked as the pressure in the cell is decreased. These observations explain why experiments made with a Kohlrausch bridge failed to show any variation of resistance with pressure. The small currents used in bridge work would not be sufficient to build up any appreciable resistance layer during the time occupied by one half cycle of the alternating current used, and the effect of one half cycle would be destroyed by the succeeding half cycle.

The currents through the gas layer are, of course, much greater than those usually associated with gaseous conduction. The charged ions are, however, supplied by the electrolytic solution, where they are present in very large numbers. For a given electrolyte the number of free ions per unit volume is approximately proportional to the specific conductivity. The specific conductivity of the gas layer should thus be proportional, for a given electrolyte, to that of the solution, as we have shown to be the case. The problem is obviously more complicated when the nature of the electrolyte is changed, as both the mobility of the ions and the thickness of the gas layer may be expected to alter with a change in the nature of the liberated ions.

We return now to the original problem as to the nature of the large extra resistance which appears in the cell when the current density exceeds a certain critical value. On the strength of the experiments described in the preceding paragraphs, we assume as our starting point that there is a transfer resistance at the interface between the electrolyte

and the electrode which consists of a very thin film of gas. This gas-film will be heated by the current passing through it, and as the mass of the gas layer is small, its temperature will rise rapidly until the heat losses due to conduction and radiation balance the input of energy by the current. The temperature of the layer will increase as the current is increased, and may for large current densities be much higher than the boiling-point of the solution. The conditions now are essentially similar to those which obtain when a drop of water is placed on a red-hot platinum dish, and we suggest that at a certain critical current density the liquid passes into the spheroidal state, and becomes separated from the electrode by a cushion of superheated vapour. It is the formation of this cushion of vapour, which may be many times thicker than the initial gas layer, which causes the sudden increase in resistance of the cell when a certain current density is exceeded.

Before proceeding to bring forward further evidence in support of this hypothesis, we may perhaps explain why it was thought necessary to assume that the heat was developed in a transfer resistance rather than in the liquid in contact with the electrode, or in the electrode itself. The very large current densities at the point electrode produce very considerable heating in the adjacent liquid, and the currents of hot liquid flowing away from the point can readily be seen if the cell is projected on a screen by an optical lantern. In the absence of an intervening layer, however, the liquid would simply boil at the electrode when its boiling-point was reached, forming bubbles of steam which would interrupt the current momentarily but would not give rise to a steady highly resistant stage. This is, in fact, exactly what happens if a non-polarizable electrode, such as a copper wire in copper sulphate solution, is employed. After a certain current density is reached there is a rapid evolution of steam-bubbles from the surface of the wire and the ammeter fluctuates wildly, but it was not found possible to produce the phenomenon of the steady highly resistant stage. This formation of steam-bubbles by passing a current through a narrow constriction in the liquid is used to produce interruptions in the current in a Caldwell interrupter.

It seemed even clearer that the effect was not due to the heat developed by the current in the electrode. The resistance of a short thick anode is much less than that of a long thin electrode of equal area, but the critical

current was the same for both. As an additional verification, however, a hollow electrode of thin platinum was used and its temperature, when the cell was in the highly resistant state, was taken by a thermo-junction placed in contact with its interior. The temperatures recorded varied from 99°·5 C. to 107° C. according to the voltage applied to the cell. These temperatures are too low to produce the spheroidal state in an aqueous solution. When the electrode is a thin wire higher temperatures than these are undoubtedly reached, and the wire may even become red hot. The experiments described, however, show that this is not a necessary condition for the formation of the resistant film.

The appearance of the electrode when the cell was in the highly resistant state indicates clearly that the liquid is not in contact with the metal, and the characteristic sound emitted by the cell when the current is cut off, and which may best be represented by "zip," suggests that the intervening layer consisted of steam. Although the heating of the electrode is not the primary cause of the steam layer, raising the temperature of the electrode ought to facilitate the passage into the spheroidal state. An anode was therefore made in the form of a loop, so that it could be heated by passing a current through it independently of the current through the cell. The resistance of the platinum loop was small, so that the heat which could be generated in it was small compared with that generated in the cell. It was found possible, however, by using large currents in the loop, to reduce the critical current required to throw the cell into the resistant state by as much as 20 per cent.

Further evidence is provided by experiments made with different solvents. The minimum temperature for the heating surface to produce the spheroidal condition becomes lower as the boiling-point of the liquid is lower. For water it is about 200° C.; for alcohol about 135° C. For solutions of the same electrolyte and of equal conductivity the critical current should therefore be less for alcoholic than for aqueous solutions. Using sodium hydrate as the electrolyte, the critical current for an aqueous solution was 3·6 amperes, and for a solution of equal conductivity in methyl alcohol it was 2·7 amperes. Using aniline hydrochloride as the electrolyte, an aqueous solution gave 5·4 amperes as the critical current, and an alcoholic solution 3·2 amperes. Assuming that the temperature of the layer is roughly proportional to the square of the current, these values agree sufficiently well with what might be expected, on the hypothesis that we are dealing with the spheroidal state.

In our previous paper we mentioned that when the cell had passed into the resistant state increasing the voltage across the cell resulted in an actual diminution of the current. Some measurements of this effect are contained in Table IV. These measurements refer to sulphuric acid (S.G. 1·20) at atmospheric pressure. It will be seen that the current falls from 0·675 ampere to 0·20 ampere as the voltage across the cell is increased from 62 to 208 volts. It will be seen also that the product of current

TABLE IV.

Current and voltage in the highly resistant stage. Sulphuric acid (S.G. = 1·20).

| Voltage. | Current. | Watts. |
|---|---|---|
| 62 | ·675 | 41·8 |
| 72 | ·575 | 41·5 |
| 77 | ·540 | 41·5 |
| 92 | ·465 | 42·8 |
| 208 | ·200 | 41·6 |

into voltage remains approximately constant, that is to say, the power dissipated in the cell is practically constant at all voltages. Since the electrolytic resistance is quite small (about 1 ohm in this example) this power is practically all expended in the resistant layer. Thus, the expenditure of energy in the layer remains constant. On the hypothesis we have put forward, the system is in equilibrium when the hydrostatic pressure on the film is exactly balanced by the pressure due to the superheated steam within it. If it were possible to increase the temperature of the steam the equilibrium would be destroyed. On applying an increased voltage to the cell the layer expands, thus increasing the resistance and diminishing the current until the expenditure of energy is reduced again to the equilibrium value.

It may be pointed out that the power required to maintain the spheroidal condition is considerably greater than that expended in the cell at what we have called the critical point. If the voltage across the cell is made somewhat greater than the critical voltage the current through the cell is reduced, but both ammeter and voltmeter show violent fluctuations. Oscillograms of the current show that at this stage the cell is fluctuating irregularly, and often very

rapidly, between the conducting and the resistant states. Apparently the liquid at the electrode assumes momentarily the spheroidal condition, but this condition does not become permanent until the rate of expenditure of power is still further increased.

*Summary.*

Evidence is brought to show that a contact or transfer resistance exists between an electrolyte and a polarizable electrode immersed in it.

This resistance is shown to be inversely proportional to the pressure on the cell. From this it is deduced that the transfer resistance consists of a thin gas-film.

If the current density exceeds a certain critical value the resistance at the electrode is very largely increased. It is suggested that this is due to the liquid being thrown into the spheroidal state by the heat generated in the transfer resistance owing to the passage of the current through it.

University College,
Reading.
June 26, 1925.

---

## CXVI. *A Note on the Summation Rules for the Intensities of Spectral Lines.* *By* R. H. Fowler*.

1. *Summary.*—It is the object of this note to give as accurate a theoretical interpretation as possible of the well-known summation rules of Ornstein, Burger and Dorgelo by a refined † application of the Correspondence Principle, in order to see in what sense the summation rules are to be interpreted when applied to associated lines whose frequency differences are not entirely negligible.

It is shown that if the intensities are reckoned in numbers of quanta per second, then the summation rules ought to be fulfilled to the degree of accuracy with which the Fourier coefficients of the original electronic system are left unaltered by the superposed perturbation which splits the radiation up into the associated group of lines.

2. *Emission.*—Consider an electronic system whose electrical moment in a selected stationary state is described by

* Communicated by the Author.
† Heisenberg, *Zeit. für Phys.* xxxi. p. 617 (1925).

the complex vector M,

$$\mathrm{M} = \tfrac{1}{2} \sum_{-\infty}^{+\infty} \mathrm{C}_\tau e^{2\pi i \tau\omega} \quad (\mathrm{C}_\tau = \overline{\mathrm{C}}_{-\tau}), \quad . \quad . \quad . \quad (1)$$

where $\tau\omega$ is the shortened form of $\tau_1\omega_1 + \ldots + \tau_s\omega_s$, and the summation is over all integral values of the $\tau$'s. Suppose that a new frequency $\sigma$ is imposed as a perturbation on this motion, by making the electronic system rotate as a whole about a new axis, but that relative to the rotating axes the motion is still exactly described by unaltered coefficients $\mathrm{C}_\tau$. Some such picture forms the base of any such discussion of intensities. It is well known that the terms in M of a single frequency $\tau\omega$ split up into vector terms of three frequencies represented by

$$\tfrac{1}{2}\mathrm{C}_1 e^{2\pi i(\tau\omega+\sigma)}, \quad \tfrac{1}{2}\mathrm{C}_2 e^{2\pi i(\tau\omega-\sigma)}, \quad \tfrac{1}{2}\mathrm{C}_3 e^{2\pi i\tau\omega},$$

which are such that exactly

$$\mathrm{C}_1\overline{\mathrm{C}}_1 + \mathrm{C}_2\overline{\mathrm{C}}_2 + \mathrm{C}_3\overline{\mathrm{C}}_3 = \mathrm{C}_\tau\overline{\mathrm{C}}_\tau. \quad . \quad . \quad . \quad . \quad (2)$$

On the classical theory the rate of emission $\mathrm{E}_1$ of energy of frequency $\tau\omega+\sigma$ is

$$\frac{(2\pi)^4}{3c^3}\mathrm{C}_1\overline{\mathrm{C}}_1(\tau\omega+\sigma)^4.$$

It follows in view of (2) that

$$\frac{\mathrm{E}_1}{\nu_1^4} + \frac{\mathrm{E}_2}{\nu_2^4} + \frac{\mathrm{E}_3}{\nu_3^4} = \frac{\mathrm{E}}{\nu^4}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

say, or that $\Sigma\mathrm{E}/\nu^4$ is independent of $\sigma$ and of the orientation of the axis of $\sigma$. The quantity which in the quantum theory corresponds to $\mathrm{E}_1$ is $\mathrm{A}_1/h\nu_1$, where $\mathrm{A}_1$ is Einstein's emission coefficient. It seems therefore to be the proper refined application of the Correspondence Principle to assert that

$$\frac{\mathrm{A}_1}{\nu_1^3} + \frac{\mathrm{A}_2}{\nu_2^3} + \frac{\mathrm{A}_3}{\nu_3^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

is independent of the new frequency $\sigma$ and of the orientation of its axis with respect to the original axes of the electronic system.

3. *Absorption.*—Van Vleck * has shown that the classical rate of absorption of energy of frequency $\tau\omega$ by the normal

* Van Vleck, Phys. Rev. xxiv. p. 347 (1924); in particular p. 358, eqn. (38).

electronic system is

$$\tfrac{2}{3}\pi^3\left(\tau\frac{\partial}{\partial \mathrm{J}}\right)\{\mathrm{C}_\tau\bar{\mathrm{C}}_\tau\tau\omega\rho(\tau\omega)\}, \quad . \quad . \quad . \quad . \quad (5)$$

where $\left(\tau\dfrac{\partial}{\partial \mathrm{J}}\right)$ is the shortened form of $\tau_1\dfrac{\partial}{\partial \mathrm{J}_1}+\ldots+\tau_s\dfrac{\partial}{\partial \mathrm{J}_s}$, and $\rho(\nu)$ is the radiation density of frequency $\nu$. When the $\sigma$-perturbation is imposed this changes to three terms of the form

$$\tfrac{2}{3}\pi^3\left(\tau\frac{\partial}{\partial \mathrm{J}}+\frac{\partial}{\partial \mathrm{J}'}\right)\{\mathrm{C}_1\bar{\mathrm{C}}_1(\tau\omega+\sigma)\rho(\tau\omega+\sigma)\}, \quad . \quad (6)$$

where J′ is the generalized momentum conjugated to $\sigma$.

The transfer from the classical to the quantum theory is here somewhat less obvious, but there seems to be little doubt, in view of recent work *, as to the correct analogy. We replace differentials by differences so that the analogue of (5) or (6) is

$$\mathrm{B}h\nu\rho(\nu)-\mathrm{B}'h\nu'\rho(\nu'),$$

where B and B′ are Einstein's coefficients for absorptive and induced emissive switches of the same quantum intervals from the given initial state. By considering a suitable special field of radiation in which $\nu\rho(\nu)$ is constant, we see at once that the analogue of the fact that (2) is true when the new frequency is imposed must be that

$$\Sigma\mathrm{B}-\Sigma\mathrm{B}'$$

is independent of $\sigma$ and its orientation.

4. *The summation rules.*—Now the A's and B's of a given switch $r\longrightarrow s$ are connected by Einstein's relations

$$\varpi_r\mathrm{A}_{rs}=\frac{8\pi h\nu^3{}_{rs}}{c^3}\varpi_r\mathrm{B}'_{rs}=\frac{8\pi h\nu^3{}_{rs}}{c^3}\varpi_s\mathrm{B}_{sr}\ , \quad . \quad . \quad (7)$$

where $\varpi_r$ and $\varpi_s$ are the statistical weights of the end states $r$ and $s$. Hence the constancy of $\Sigma\mathrm{A}/\nu^3$ implies also the constancy of $\Sigma\mathrm{B}'$. The refined application of the Correspondence Principle therefore leads to exact summation rules under the given postulate in the form :

(i.) $\Sigma\mathrm{A}/\nu^3$ is constant for all the upper states of a group of multiple switches ;

(ii.) $\Sigma\mathrm{B}$ is constant for all the lower states.

* Van Vleck, *loc. cit.* ; Kramers & Heisenberg, *Zeit. für Phys.* xxxi. p. 681 (1925).

The A's and B's are Einstein's coefficients and are definite constants of the atom.

If we now introduce the statistical weights of the terminal states and write $b = \varpi B$, where $\varpi$ is the weight of the state from which the absorption switch characterized by B starts, then (ii.) becomes

($\alpha$) $\frac{\Sigma b}{\varpi}$ is constant for all states of the lower group,

and in virtue of (7) (i.) becomes

($\beta$) $\frac{\Sigma b}{\varpi'}$ is constant for all states (weights $\varpi'$) of the upper group.

The statements ($\alpha$) and ($\beta$) are the general forms of the summation rules. The $b$'s are proportional to the absorption cœfficients (in numbers of quanta) which would be observed at infinite temperature.

5. The point of this note lies in this, that the summation rules expressed in terms of the B's or $b$'s should be exact, whatever the frequency differences, provided only that the perturbation which splits the level leaves the $C_\tau$ of (1) unaffected. The summation rules should then hold exactly for observed intensities when these are expressed in terms of *numbers of quanta per atom per second*. More generally one should expect the summation rules as here interpreted to remain true, with deviations from exactness of the same order as the relative changes in the $C_\tau$. If for example these changes are second order in $\delta\nu/\nu$ or $\sigma/(\tau\omega)$, then the deviations from the summation rules will be of the second order.

It is actually true for certain mechanical models that the changes in the $C_\tau$ are of the second order. For example this will hold for the Zeeman effect, where the only first order effect of the applied magnetic field is to impose on the electronic motion as a whole (some multiple of) the Larmor rotation. The core-series electron model of the atom, with both core and series electron precessing about the axis of resultant angular momentum under their mutual interaction, is rather too indefinite for a confident prediction of second order accuracy in this case too, but it might perhaps be expected.

For an oscillating dipole (model of a molecule) on which rotations are imposed we should certainly obtain this second order accuracy. The radial oscillations (whatever their form) are modified only by the centrifugal force which is of the

second order in $\sigma$. Relative to the proper uniformly rotating axes the oscillations are no longer linear, but acquire a looped form, with a component at right angles to the main motion proportional to $\sigma$. This leads to new terms in $C_r\bar{C}_r$, but proportional still only to $\sigma^2$.

There seems, therefore, in general to be theoretical reason to expect greater accuracy of the summation rules than has appeared in former discussions.

---

## CXVII. *On the System of Vortices generated by a Circular Cylinder in Steady Motion through a Fluid.* *By* C. N. H. Lock, *M.A., of the Aerodynamics Department, National Physical Laboratory* *.

### 1. *Introduction.*

IN discussing the uniform motion of an infinite circular cylinder through an incompressible fluid of moderate viscosity, Kármán has suggested † that the wake left behind by the cylinder takes the form of a double row of two-dimensional vortices. He has employed this conception of the flow pattern to calculate the resistance of the cylinder in terms of the period and velocity of the vortices which he observed in the wake of a cylinder dragged through water, and he obtained values of resistance agreeing well with observation. His observed values of the resistance and period of the vortices are also in fair agreement with those obtained by Relf in both air and water at corresponding values of $VL/\nu$ ‡.

It therefore seems worth while to apply Kármán's theory as far as is possible to the recent results for higher values of $VL/\nu$ described by Relf and Simmons §, and especially to

* Communicated by Mr. R. V. Southwell, F.R.S., by permission of the Aeronautical Research Committee.

† Kármán u. Rubach, "Flüssigkeits- und Luftwiderstand," *Physik Zeitschr.* vol. xiii. p. 49 (1912). Also:—Lamb, 'Hydrodynamics,' 4th Edn. p. 219.

‡ Relf, "On the Sound emitted by Wires of Circular Section when exposed to an Air-Current," Phil. Mag. ser. 6, xlii. p. 173 (1921).

Throughout the present note, L is the diameter of the cylinder, V its velocity relative to the fluid, and $\nu$ the kinematic coefficient of viscosity.

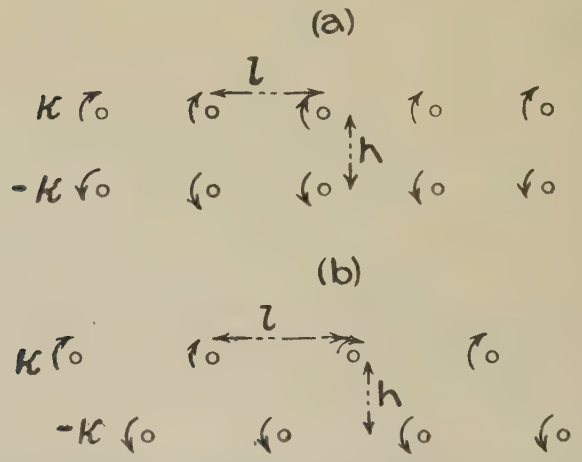
§ Relf and Simmons, "The Frequency of the Eddies generated by the Motion of Circular Cylinders through a Fluid," Phil. Mag. vol. xlix. p. 509 (1925).

examine its bearing on the sudden change in the resistance and frequency coefficients observed in the neighbourhood of $(VL/\nu = 3 \times 10^5)$.

## 2. *The System of Vortices in a Perfect Fluid in Two Dimensions.*

Kármán * first of all discusses the stability of the two possible equilibrium arrangements of two-dimensional vortices in double rows shown in fig. 1: (*a*) a symmetrical double row, and (*b*) an unsymmetrical double row. In both systems the individual vortices of the two rows have equal and opposite strengths $\kappa$ and $-\kappa$, the distance between the rows is $h$ and the distance between the consecutive vortices of the same row $l$.

Fig. 1.




He shows that the system (*a*) is unstable in all cases, while the system (*b*) is unstable except for the particular value of the ratio $h/l$ given by the equation

$$\cosh \frac{2\pi h}{l} = 2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for which it is stable. He concludes that the flow at a sufficient distance behind a cylinder is of this type, and this conclusion is well supported by photographs and visual observations in water, the eddies being formed alternately on either side of the cylinder.

The system of eddies will move parallel to its length with a velocity $u$ relative to the surrounding fluid, which

* Kármán u. Rubach, "Flüssigkeits- und Luftwiderstand," *Physik.* &c.

is given in terms of $\kappa$ by the formula

$$u = \frac{\kappa}{2l} \tanh \frac{\pi h}{l}, \text{ case } (b). \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For the stable case this reduces, in virtue of equation (1), to

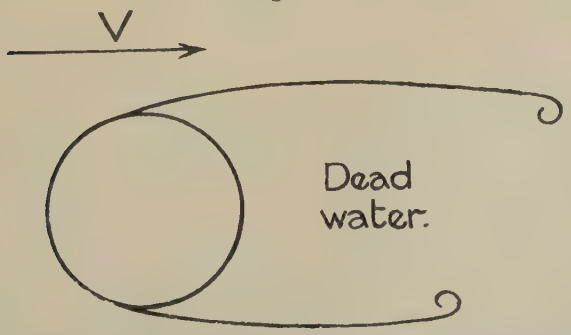
$$u = \frac{\kappa}{l\sqrt{8}} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The system is thus completely determinate when the values of two variables are known, *e.g.*, either $\kappa$ and $l$, or $u$ and $l$. In practice it is necessary to connect these quantities with the velocity V and diameter L of the cylinder which causes the motion. If this can be done, the resistance of the cylinder can be determined by integrating the mean rate of flow of momentum into and out of certain regions and the pressure over the boundaries of these regions. The regions chosen are bounded by straight lines perpendicular to the direction of motion at large distances in front of and behind the cylinder. By this method Kármán obtains the following formula for the mean resistance of the cylinder per unit length :—

$$R = \rho\kappa \frac{h}{l}(V - 2u) + \rho \frac{\kappa^2}{2\pi l} . \quad . \quad . \quad . \quad . \quad (4)$$

It might be mentioned here that an approximate relation between the strength of a vortex and the velocity of the cylinder could be obtained from the following considerations. If the wake of the cylinder consisted of a dead water region bounded by surfaces of discontinuity, as in

Fig. 2.




the Kirchhoff solution for a flat plate, the strength of each vortex sheet bounding the dead water region would be equal to V. Assuming that the vortex sheets become unstable and ultimately break up into the Kármán system of vortices (see fig. 2), then the total strength of the

vortices formed in a given interval of time would be equal to the strength of the vortex sheets passing a fixed point in the same interval, or

$$V = \frac{\kappa}{l}.$$

In practice no discontinuous sheet is formed, but it seems reasonable to suppose that the last formula will still give an upper limit to the possible strength of the vortices.

### 3. *Experimental results.*

In applying these results Kármán observed both the period and the velocity of the system of vortices, by means of photographs of the flow produced in water by moving a cylinder through it. The period T represents the interva between the instants at which two vortices of the same row pass a point *fixed relative to the cylinder*; this is equal to the interval between the throwing off of successive vortices from the same side of the cylinder. Hence we have the relation

$$T = \frac{l}{V-u}.$$

Kármán obtains the following values for a cylinder of diameter 1·5 cm., moving with velocities 11·0 cm./sec. and 15·8 cm./sec. :—

$$VT = 7{\cdot}4 \text{ cm.}$$

$$u/V = 0{\cdot}14.$$

This value of $u/V$ gives the value

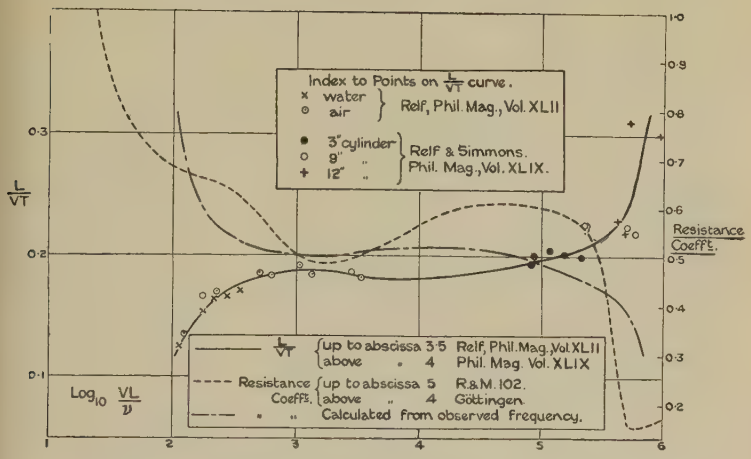
$$\frac{\kappa}{lV} = 0{\cdot}40.$$

In Relf's experiments the values of $u$ were not determined. We shall assume that the value obtained by Von Kármán for $\frac{u}{V}$ or $\frac{\kappa}{lV}$ may be applied, and that it is independent of $\frac{VL}{\nu}$.

Fig. 3 shows curves of observed frequency and resistance, plotted against $\frac{VL}{\nu}$ in the form of coefficients $\frac{R}{\rho V^2 L}$ and $\frac{L}{VT}$; these have been taken from the paper by Relf and

Simmons previously referred to *. From the observed frequency it is possible to calculate the resistance by Kármán's formula, assuming the constant value 0·4 given

Fig. 3.


Index to Points on $\frac{L}{VT}$ curve.
× water
⊙ air
Relf, Phil. Mag., Vol. XLII
● 3" cylinder
○ 9" "
+ 12" "
Relf & Simmons. Phil. Mag., Vol. XLIX.
$\frac{L}{VT}$
Resistance Coeff$^t$.
$\log_{10} \frac{VL}{\nu}$
$\frac{L}{VT}$ up to abscissa 3·5 Relf, Phil. Mag. Vol. XLII
above " 4 Phil. Mag. Vol. XLIX
Resistance Coeffs. up to abscissa 5 R.&M. 102.
above " 4 Göttingen.
" " Calculated from observed frequency.

by Kármán's experiments for the coefficient $\frac{\kappa}{lV}$. The results, which are shown by the chain-dotted line, indicate that complete agreement would involve only slight changes in this coefficient, except at very low $\frac{VL}{\nu}$, where the coefficient presumably tends to zero.

## 4. *Conclusions.*

Various results bearing on the present problem have been obtained from the theory of viscous flow. At very low values of $\frac{VL}{\nu}$ we have the approximate solution of the viscous equations by Oseen's method given by Lamb†; this is a non-periodic motion, and gives a resistance varying approximately but not exactly as the first power of the velocity.

* The curve of resistance coefficient was taken from tests of the resistance of wires made at the National Physical Laboratory (Advisory Committee for Aeronautics, R. & M. 102) up to $VL/\nu = 10^4$, and from experiments made at Göttingen (*Physik. Zeitschr.* 1921, p. 332) for higher values of $VL/\nu$. The values of observed frequency were taken from the paper by Relf cited above (Phil. Mag. xlii.) up to $VL/\nu = 10^4$ and from the paper by Relf and Simmons (Phil. Mag. xlix.) for higher values of $VL/\nu$.

† Lamb, 'Hydrodynamics,' 4th Edn. p. 605.

At the other extreme, for large values of $\frac{VL}{\nu}$, we have the theory of the boundary layer of Prandtl and Boussinesq *. According to this theory the effect of viscosity is confined at the front of the body to a narrow layer of rotational motion, the fluid being at rest close to the body and moving irrotationally outside the layer. The development of the theory is extremely difficult, but different approximate methods agree in indicating that the vortex layer will leave the surface of the cylinder at a definite point. Different methods are not, however, very consistent in their prediction of the exact point of departure, which has been given as less than 90° and about 120° respectively from the forward point of bifurcation †.

It seems clear, however, that a thin vortex layer leaving the surface of the body provides a mechanism which is capable of giving rise to a Kármán system of vortices, and that the scale of the system produced, and therefore the drag of the body, will depend on the exact point at which the layer leaves the surface, being less the further back this point is. According to either boundary layer theory the position of this point is independent of $\frac{VL}{\nu}$ for sufficiently large values of this variable, but the uncertainty of the results makes it seem reasonable to assume that for lower values of $\frac{VL}{\nu}$ the position of the point may vary with $\frac{VL}{\nu}$, possibly in a critical manner.

The experimental values of the resistance shown in fig. 3 are consistent with steady viscous flow of the Oseen type at very low values of $\frac{VL}{\nu}$, changing gradually, as $\frac{VL}{\nu}$ increases, into the Kármán type, in which the vortices, at first very weak and far apart, gradually increase in strength until the system reaches a fairly steady state in the neighbourhood of $\frac{VL}{\nu} = 2 \times 10^3$ (corresponding to Kármán's values of 0·4 for the coefficient $\frac{\kappa}{lV}$, and 0·2 for the coefficient $\frac{L}{VT}$).

* "Stationary Streaming caused by a Body in a Fluid with Friction." By J. M. Burgers. *Koninklijke Akademie Van Wetenschappen te Amsterdam*, vol. xxiii. No. 8.

† Burgers, *loc. cit.* p. 25.

The conclusion from the recent results for higher values of $\frac{VL}{\nu}$ seems to be, not that the Kármán regime ceases to apply, but that the sudden drop in resistance at $\frac{VL}{\nu} = 4 \times 10^5$ corresponds to a sudden increase of frequency and decrease of the distance between the rows from 1·20 D to 0·7—0·5 D; this is presumably due to a sudden shift backwards of the point on the cylinder at which the boundary layer leaves the surface.

In order to verify this result completely, it would be necessary to determine the value of $l$ experimentally, and if possible to observe the details of the flow both near the cylinder and at a distance behind it.

The above argument suggests how it is possible that at high values of $\frac{VL}{\nu}$ the viscosity can modify the resistance coefficient without directly affecting the flow, except in the immediate neighbourhood of the body. The argument is confirmed by the case of the flat plate, in which the flow is entirely determined by the existence of sharp edges, and the resistance is independent of $\frac{VL}{\nu}$ except at very low values of this variable.

---

CXVIII. *Experiments on the Absorption of the Balmer Lines in Hydrogen.* *By* Ruby V. Jolowicz (*née* Wagner), *M.Sc.**

WHEN hydrogen is subjected to bombardment by electrons of sufficient energy, the molecule will be dissociated and one or both of the atoms excited, the electron being displaced from its normal orbit to one of the outer orbits, or removed out of the atom entirely. An excited atom in returning to its normal condition will emit its characteristic radiation; in the case of the hydrogen atom, when an electron returns from an outer to its inmost orbit a line of the Lyman series is emitted. If, however, the electron falls back into the second orbit instead of the first, one of the Balmer lines will be emitted instead of one of the Lyman series. A hydrogen atom whose electron is revolving in the second orbit is, then, in a condition to absorb a line of the Balmer

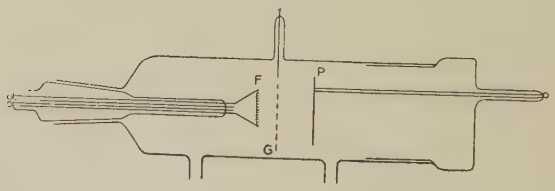
* Communicated by Prof. W. Wilson, F.R.S.

series. An attempt was made, in the experiments here described, to observe absorption of the Balmer lines by hydrogen subjected to bombardment by electrons from a glowing filament. It was expected that absorption would set in, or be suddenly increased when the potential accelerating the electrons reached certain critical values

Electrons from a glowing tungsten filament were accelerated through a grid into a field-free space between the grid and plate. A beam of light passed through the tube between grid and plate into a spectroscope, and was observed directly and also photographed. Experiments were carried out both with white light and with the light from a hydrogen discharge-tube, neutral glass wedges of two types being employed for the comparison of intensities, after the method of Nicholson and Merton*. Owing to the uneven running of the discharge-tube, it was not possible to make comparisons between the intensities of the lines photographed in two successive exposures, and a method was devised by which this difficulty was overcome.

In the preliminary experiments a small tube was used, as shown in the diagram (fig. 1). The tube was 15 cm. long

Fig. 1.




and 4 cm. in diameter. It was closed at each end by a ground-glass joint, the plate and filament being fused into the stoppers to enable them to be removed readily. The plate P was a circular copper disk 3 cm. in diameter, mounted on a copper rod, with platinum contacts through the glass. Two copper rods similarly fixed served to support the filament F, which consisted of a thoriated tungsten spiral about $1\frac{1}{2}$ cm. long. The grid G was a copper gauze disk, the same size as the plate, and fused into a side tube at the centre of the tube, $\frac{3}{4}$ cm. from the filament and $1\frac{1}{2}$ cms. from the plate. The tube was connected through calcium chloride and phosphorus-pentoxide drying tubes

* Nicholson and Merton, Phil. Trans. A, ccxvi. p. 459 (1916).

to a Gaede rotary mercury pump, backed by a Fleuss Geryk oil-pump. Pressures were read on a McLeod gauge. A palladium tube was fused into the glass, and hydrogen was obtained by diffusion through this tube. As this process is very slow, and the volume to be filled rather large, it was later found better to use hydrogen obtained by the electrolysis of barium hydroxide solution, and dried over calcium chloride and phosphorus pentoxide. The pressure of the hydrogen in the tube was varied from about 0·5 mm. to 5 mm.

A Nernst lamp with a thin paper covering over the lens of the holder was used as source of white light, and the photographs were taken with a Hilger constant deviation spectrometer, on Wratten and Wainwright's allochromatic plates. The grid and plate were connected, and accelerating voltages between filament and grid, varying from 15 volts to 50 volts, were applied. The intensity of the light was varied by altering the thickness of the screen, and exposures were made ranging from 20 minutes to 2 hours. A small discharge-tube containing hydrogen was used for a comparison spectrum. No trace of absorption lines could be found on any of the plates.

The wedge method of Nicholson and Merton was then employed, a neutral wedge being fixed in front of the spectrometer slit. The lines photographed will appear on the plate bright at one end, corresponding to the thin end of the wedge, and gradually fade off, the length of a particular line on the plate depending on its intensity. If there is any absorption of a certain line in a continuous spectrum, this would show itself by a shortening of the corresponding line on the plate or a discontinuity in the bounding curve. From the negatives obtained, positives were printed by contact, on Imperial Process plates, and enlargements made on bromide paper through a ruled process screen placed immediately in front of the paper. The screen was obtained from Messrs Vaus and Crampton, and was a full-plate photograph of one of their process plates with 100 rulings to the inch. The image obtained consisted of a number of small dots 1/100 inch apart. As the absorption of the wedge and the sensitivity of the plate depend on the wave-length, the bounding curve of the darkened patch in the case of white light was not a straight line, but a continuous curve, and any discontinuity would therefore be shown by the absence of certain dots. Three wedges were used ; two, made by Messrs. Hilger, of neutral tinted glass of different density gradients. The third was made by Ilford's Ltd., of gelatine solution cast on glass in wedge form

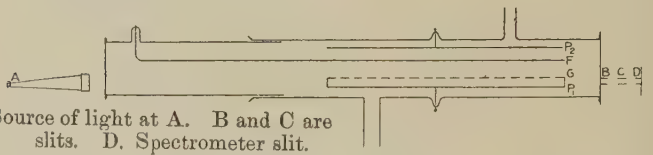
and allowed to dry. No irregularities indicating absorption were found in the outlines of any of the curves obtained.

The hydrogen lines from a discharge-tube were then photographed in the same way, the time of exposure and strength of field being varied as before; it was not possible, however, to maintain the discharge sufficiently uniform for comparisons of intensity to be made between two successive exposures, the differences in the lengths of the lines as obtained by Merton's method being inconclusive.

It was thought that the failure of the method might be due to the fact that the absorbing column of the gas was too short for the effect to be discernible. A new tube was designed in which this column was ten times as long as previously. The tube (fig. 2) was 5 cm. in diameter and 50 cm. long, and was constructed in two parts, fitted together

Fig. 2.

(*a*) Horizontal section of tube.




Source of light at A. B and C are slits. D. Spectrometer slit.

(*b*) Vertical section, showing arrangement of the long V-shaped filament.

by means of a ground-glass joint. The gallium filament F was supported by three aluminium rods in thin glass tubing, fused into one-half of the tube, platinum wires being connected to the aluminium rods and brought through the glass in the usual way. The rods were arranged so that the filament itself was entirely within the other half of the tube, and clear of the ground-joint, on account of the high temperature. The filament was V-shaped, the central supporting rod being 25 cm. longer than the outer ones, the total length of the filament being about 50 cm. At the end of the long rod there was a double hook of thin copper wire, over which the filament passed, and contact was thus made with the central rod, so that the two halves of the

filament could be used separately or together. The glass tubing over the rod prevented short circuiting of the filament in case this sagged and dropped on to the support. The plates and grid were fused into the other half of the tube. Grid G and plate $P_1$ were rigidly connected together; G was a sheet of iron gauze 26 cm. long and $3\frac{1}{2}$ cm. wide; $P_1$ was a piece of aluminium sheeting of the same size, the two being connected together at the corners and along the sides by aluminium rods 1 cm. long. $P_2$ was a similar piece of aluminium sheeting on the opposite side of the filament, slightly curved to fit into the tube. This was used to reverse the field and remove all electrons emitted by the filament from the space between F and $P_1$. The tube was at first closed at the ends, which were made as plane as possible; this was found unsatisfactory owing to the distortion, and the ends of the tube were then cut, flattened into a flange, and ground, and glass plates were sealed on with sealing-wax, soft red wax being used to protect the surface.

Every precaution was taken to remove water-vapour and impurities in the hydrogen, a charcoal tube immersed in liquid air being added in order that higher vacua could be obtained when cleaning out the tube; a liquid-air trap was also inserted. The tube was evacuated, and the central part containing the electrodes baked at about 180°. Higher temperatures could not be used owing to the buckling of the electrodes. The tube was then rinsed out repeatedly with hydrogen; as high a vacuum as possible was obtained, and the filament was allowed to glow for some time. Hydrogen was then admitted at the required pressure, and the photographs taken as with the small tube, using Ilford's Panchromatic plates. The light passed through the bulb between grid and plate as before; two slits were interposed in the path of the beam, between the tube and the spectrometer. The actual column of hydrogen subjected to electron bombardment was over 25 cm. in length *.

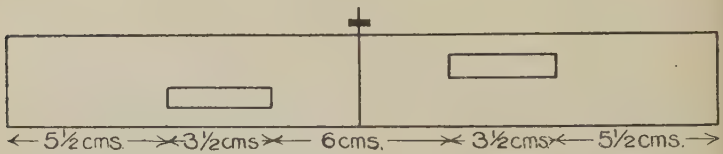
A preliminary photograph was taken with no source of light at A (fig. 2) and with the filament glowing, to ascertain whether any light from the filament passed into the spectrometer either directly or after reflexion from the walls of the tube. After 20 minutes exposure no trace was found on the plate. A comparison spectrum was taken of a hydrogen tube placed between the tube and the spectro-

* With these filaments the fall in potential along the wire is considerable; for quantitative measurements a large number of short filaments in parallel would have to be substituted.

meter; this was then removed, and two photographs of the white source (focussed on the slit) were taken, one with an accelerating field between F and $P_1$, and the second with the field between F and $P_2$. The pressure was varied from 0·1 mm. to 1 mm., and exposures from 5 mins. to 45 mins. were made. The experiments made were similar to those carried out with the small bulb, but in no case could any trace of absorption be found on any of the photographs.

Finally the light from the hydrogen discharge was passed through the tube and examined. In order to eliminate errors due to the uneven running of the discharge-tube, it was arranged that the two photographs (with and without accelerating fields between F and $P_1$) should be taken concurrently, a pendulum arrangement being used to effect this. The pendulum was made to swing across the end of the tube, between the end-plate and the spectrometer, in a plane perpendicular to the axis of the tube. The bob consisted of a long rectangular sheet of brass (fig. 3) with two

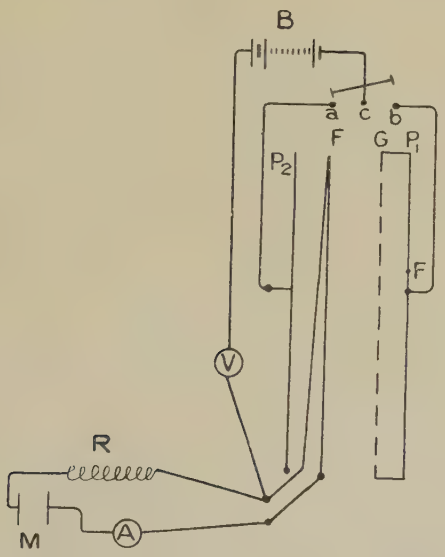
Fig. 3.




windows, as shown. A brass plate with two holes, one vertically above the other, was fitted in front of the spectrometer slit, and as the pendulum swung backwards and forwards, first one and then the other of these holes was illuminated. At the same time there was a lever arrangement at the upper end of the pendulum with three platinum contacts dipping into mercury cups. The centre contact was permanently connected to the positive pole of the high-tension battery, and the other two to the plates $P_1$, $P_2$ respectively. The negative terminal of the battery was permanently connected to the filament. As the pendulum swings, $P_1$ and $P_2$ are alternately connected to the battery, and the exact moment of reversal of the field can be accurately adjusted by means of the movable platinum contacts, with the help of a voltmeter between plate and filament (see fig. 4). The adjustment was made so that the field was reversed at the moment when the pendulum was in the central position, and no light fell on to the spectrometer slit. The pendulum was actuated by clockwork, and

the period of swing was about 2·3 secs. The bob itself could be inverted, the two windows being thus interchanged. The aluminium supporting rod of the pendulum was about 100 cm. long and the vertical distance between the windows $\frac{1}{2}$ cm., so that the error introduced by the arc of swing was less than 1 per cent. The light from the discharge-tube

Fig. 4.




*a, b, c.* Lever arrangement controlled by pendulum.

B. High-tension battery. V. Voltmeter.
M. Electric mains. A. Ammeter.

was concentrated on to the slit by means of a large condenser. Two photographs were thus obtained concurrently, in one of which the absorbing column of hydrogen was activated. The times of exposure for the two photographs varied from $1\frac{1}{4}$ hours to $2\frac{1}{2}$ hours. The filament was lighted from the mains, the current being about 2·2 amps. A voltage of 30 volts was applied between the centre of the filament and the plates by means of a high-tension battery. The pressure was varied from 0·2 to 0·5 mm.

Two sets of such exposures were made in each case, in immediate succession, without turning off the filament or discharge-tube. The only alteration made in the second case was in the connexions *a* and *b* (fig. 4), which were reversed ; thus, if the direction of the field was from F to

$P_1$ when the upper window was illuminated in the first case, it was from F to $P_2$ in the second case. In this way the absorption effect alone was reversed, and errors due to unequal illumination of the slit, difference in the time of exposure through the two windows (due to the arc of swing), etc., could be eliminated.

If $A_1$, $A_2$ are the intensities of corresponding lines in the two spectra obtained in the first exposure, and $B_1$, $B_2$ those in the second exposure, then

$$A_1 = I,$$
$$A_2 = I + dI - \delta I \text{ approx.},$$

where I is the intensity of the light from the discharge-tube entering both windows equally; $dI$ is the intensity due to any additional light entering the upper window (this may be negative); $\delta I$ is the fraction of the light absorbed by the activated column.

Similarly,
$$B_1 = I - \delta I,$$
$$B_2 = I + dI.$$

$$\therefore \quad \frac{A_1}{A_2} = \frac{I}{I + dI - \delta I}, \quad \frac{B_1}{B_2} = \frac{I - \delta I}{I + dI}, \quad \text{and} \quad \frac{A_1}{A_2} > \frac{B_1}{B_2}.$$

By comparison of these intensities any appreciable absorption could be detected.

The photographs taken in this way were examined by means of a Moll microphotometer, and photographic records of the galvanometer deflexions indicating the intensities of the lines $H_\alpha$ and $H_\beta$ for each case were obtained (through the kindness of Messrs. Adam Hilger). These show no evidence of any absorption; and the conclusion must be drawn that the number of excited hydrogen atoms under the conditions of the experiments was very small. On the other hand, it is fairly certain that the hydrogen in these experiments was strongly ionized, since there is a marked ionization potential in the neighbourhood of 16 volts; and therefore the absence of absorption may indicate that the ionization is molecular, unaccompanied by dissociation. This inference is supported by a recent investigation of Richardson and Tanaka *, who find evidence in favour of the view that the impact ionization of hydrogen occurring at about 16 volts is of this character.

It is hoped to repeat these experiments under different conditions.

9 Ferncroft Avenue,
Hampstead, N.W. 3.

* Richardson and Tanaka, Royal Society Proc. A, vol. cvi. (1924).

# CXIX. *Secondary Effects of Shear on an Elastic Body.* *By* W. R. Dean, *M.A.**

## 1. *Introduction and Summary.*

SOME years ago the late J. H. Poynting did some experimental work on what may be termed the secondary changes in the dimensions of a loaded wire when twisted. From the existence of the pressures of light and of sound waves, he anticipated a similar pressure in the case of transverse waves in an elastic solid. A direct experimental verification being impracticable, the corresponding statical pressure was investigated. A pressure caused by transverse waves can only be due to the fact that an elastic body cannot be held in a state of simple shear by shearing forces only, a pressure (or tension) perpendicular to the planes of shear being in particular required ; without this stress, an elongation (or contraction) in the same direction will take place. Corresponding changes in dimensions will occur with a twisted wire. The experimental difficulties of observing in this case such small changes as could be expected were considerable, but consistent alterations were measured by Poynting, and the existence of a pressure due to shear inferred.

The theoretical treatment of this problem is beyond the scope of the theory of elasticity, according to which, as is well known, there is no change in the length or in the diameter of a twisted wire, and no attempt was made to predict the results of the experiments on special assumptions, more accurate than those implied by Hooke's law, as to the relations between stress and strain.

Any general theory of Elastic Stability is in the same position of demanding an extension of Hooke's law, and one such extension has been made for this purpose. By means of it equations of elasticity can be deduced to any order of accuracy that is required, and, in particular, equations adequate to deal with the problem of the twisted wire. Such equations are derived in this paper, and the results given by them are compared with those of experiment.

The comparison reveals a serious divergence. Poynting found that with light loads a wire shortened on twisting, but that with large enough loads it lengthened by an

* Communicated by Mr. R. V. Southwell, F.R.S.

amount practically independent of the load. The shortening was attributed to the original coiled configuration of the wire, and the value of the lengthening with large loads was accepted as measuring the real effect of the twist. It was deduced, that is to say, that with a wire which was actually unstrained when straight, a lengthening, independent of any load that might be applied, would be found. The extension of Hooke's law used leads to an alteration in length that is practically independent of the load, but which in the case of most bodies is a shortening *, altogether smaller than the shortening found experimentally with the lightest loads. The theoretical values for the alteration in diameter are in good agreement with those of experiment in the case of steel wires, but the agreement is poor in the case of some less important experiments on copper wires. A slightly different extension of Hooke's law is next made, which gives an alteration in length always a lengthening, and one independent, for given twist and given radius, of the material of the wire. In magnitude this is, however, in most cases not more than one-tenth of the experimental value. The alterations in radius predicted are practically the same as those of the first theory.

It was found experimentally that the secondary alterations depended on the direction of the twist, which was further evidence of initial strain. The work of this paper takes no account of this, but it appears quite impossible to get from either theory a lengthening of the right order of magnitude by assuming some initial strain. It can only be concluded that neither theory is in agreement with experimental fact. It is pointed out that the two extensions of Hooke's law made are the only satisfactory possibilities if additional elastic constants are not to be introduced. If more elastic constants are introduced, there does not appear to be sufficient experimental material available to determine them.

## 2. *The First Assumption.*

It is known from the theory of elasticity † that a circular cylinder can be held twisted by couples applied to its ends, so that any cross-section remains in its equilibrium plane,

* It is actually found that the alteration is a shortening if the value of Poisson's ratio is less than $\frac{1}{3}$, as is the case with most metals: lead, and possibly copper, are the only important exceptions.

† A. E. H. Love, 'Mathematical Theory of Elasticity' (3rd edition), § 86 (*d*).

and is turned through an angle that is a linear function of its distance from one end. If $r$, $\theta$, $z$ are the cylindrical coordinates of any point of the cylinder, $u$, $v$, $w$, the corresponding displacements of this point, are given by

$$u=0,\ v=\tau rz,\ w=0, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\tau$ is a constant which measures the twist of the cylinder. The twist is not accompanied by alteration of the cylinder in length or in diameter: to predict such secondary effects a theory must take account of terms that are of order above the first in coordinates of displacement, or rather of strains. The first necessity is accordingly some exact assumption as to the relations between stress and strain.

The first assumption * used here may be stated as follows: in a distortion of any magnitude of an elastic body, there are associated with each point of the body three linear elements which are orthogonal both before and after strain, and these elements undergo stationary extensions, the "principal strains." The stress consists of three tensions (or pressures), the "principal stresses," in the directions of these elements after strain. It is assumed that the principal stresses and strains satisfy the usual equations derived from Hooke's law; that is to say, if the principal strains are extensions $e_1$, $e_2$, $e_3$, and the corresponding principal stresses are tensions $S_1$, $S_2$, $S_3$, then

$$S_1=\frac{E}{(1+\sigma)(1-2\sigma)}[(1-2\sigma)e_1+\sigma\Sigma e_1], \text{ etc.}, \quad . \quad (2)$$

where E is Young's modulus and $\sigma$ Poisson's ratio. Extension is defined as the ratio of the increase in length of an element to its length before strain, and stress as the total action over an element of surface divided by the area of the element before strain. With this assumption equations of elasticity can be obtained to any order of accuracy that is required.

### 3. *The Extension of an Element.*

Equations (1) give a solution of the problem of the twisted cylinder that is accurate to the first power of $\tau$. To deduce the important features of the secondary effects

* Originally stated by R. V. Southwell, Phil. Trans. A, vol. ccxiii. p. 187, and applied to problems of elastic stability. A similar application of the same assumption has been made by the writer, Proc. Roy. Soc. A, vol. cvii. p. 734.

due to the twist, it is sufficient to obtain a solution accurate to the order $\tau^2$. $u$, $v$, $w$, the displacements of the point whose cylindrical coordinates are $r$, $\theta$, $z$, are defined so that the coordinates of this point after strain are

$$r+u,\ \theta+v/r,\ z+w.$$

Thus $v$ is a curvilinear displacement along a circle in a plane perpendicular to the axis of the cylinder, and $w$ is the difference between the initial and final distances of the point from the axis. So far as the first order analysis is concerned, it is immaterial whether $u$, $v$, $w$ are defined in this way, or as orthogonal linear displacements. We now write

$$u=u',\ v=\tau rz+v',\ w=w', \quad . \quad . \quad . \quad . \quad (3)$$

where $u'$, $v'$, and $w'$ are of the order $\tau^2$, and neglect terms of order higher than this in the subsequent work.

In the first place an expression for the extension of a linear element in the strain is required. Let PP′ be a linear element of length $\rho$ issuing from P, $(r, \theta, z)$, in the direction $(l, m, n)$ with regard to the $r$, $\theta$, $z$ axes at P*. Let P be displaced to $P_1$, and P′ to $P_1'$, in the strain. If the length of $P_1P_1'$ is written $\rho\,(1+e)$, it is easy to see that

$$\begin{aligned}(1+e)^2=&\left[l\left(1+\frac{\partial u}{\partial r}\right)+\frac{m}{r}\frac{\partial u}{\partial \theta}+n\frac{\partial u}{\partial z}\right]^2\\&+(1+u/r)^2\left[l\left(\frac{\partial v}{\partial r}-\frac{v}{r}\right)+m\left(1+\frac{1}{r}\frac{\partial v}{\partial \theta}\right)+n\frac{\partial v}{\partial z}\right]^2\\&+\left[l\frac{\partial w}{\partial r}+\frac{m}{r}\frac{\partial w}{\partial \theta}+n\left(1+\frac{\partial w}{\partial z}\right)\right]^2.\end{aligned}$$

This is an exact formula for the extension $e$, which reduces here, as we may suppose throughout that $u$, $v$ and $w$ are independent of $\theta$, to

$$\begin{aligned}(1+e)^2=&\left[l\left(1+\frac{\partial u}{\partial r}\right)+n\frac{\partial u}{\partial z}\right]^2\\&+(1+u/r)^2\left[l\left(\frac{\partial v}{\partial r}-\frac{v}{r}\right)+m+n\frac{\partial v}{\partial z}\right]^2\\&+\left[l\frac{\partial w}{\partial r}+n\left(1+\frac{\partial w}{\partial z}\right)\right]^2\\=&\mathrm{A}l^2+\mathrm{B}m^2+\mathrm{C}n^2+2\mathrm{F}mn+2\mathrm{G}nl+2\mathrm{H}lm. \quad . \quad (4)\end{aligned}$$

* These axes are, of course, a line through P parallel to the axis of the cylinder ($z$), a line through P perpendicular to this axis ($r$), and a third perpendicular ($\theta$).

4. *The Stress Components.*

If the direction cosines of $P_1P_1'$ with regard to $r$, $\theta$, $z$ axes at $P_1$ are $l'$, $m'$, $n'$, we have to the first order of $u$, $v$, $w$, (this accuracy is sufficient for these relations),

$$l' = \frac{1}{1+e}\left[l\left(1+\frac{\partial u}{\partial r}\right)+n\frac{\partial u}{\partial z}\right], \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$m' = \frac{1}{1+e}\left[l\left(\frac{\partial v}{\partial r}-\frac{v}{r}\right)+m\left(1+\frac{u}{r}\right)+n\frac{\partial v}{\partial z}\right], \quad . \quad (6)$$

and $$n' = \frac{1}{1+e}\left[l\frac{\partial w}{\partial r}+n\left(1+\frac{\partial w}{\partial z}\right)\right], \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $e$ is to be calculated to the first order of the displacements from (4).

Suppose that the linear elements at P which undergo the principal extensions $e_1$, $e_2$, $e_3$ have, before strain, direction cosines given by the scheme

| | $r$ | $\theta$ | $z$ |
|---|---|---|---|
| 1 ..... | $l_1$ | $m_1$ | $n_1$ |
| 2 ..... | $l_2$ | $m_2$ | $n_2$ |
| 3 ..... | $l_3$ | $m_3$ | $n_3$ |

with regard to the $r$, $\theta$, $z$ axes at P. After strain, let the direction cosines of the elements be given by

| | $\bar{r}$ | $\bar{\theta}$ | $\bar{z}$ |
|---|---|---|---|
| 1 ..... | $l_1'$ | $m_1'$ | $n_1'$ |
| 2 ..... | $l_2'$ | $m_2'$ | $n_2'$ |
| 3 ..... | $l_3'$ | $m_3'$ | $n_3'$ |

with regard to $r$, $\theta$, $z$ axes at $P_1$, whose coordinates are written $\bar{r}$, $\bar{\theta}$, $\bar{z}$. Both sets of direction cosines are then of mutually perpendicular lines. The principal stresses $S_1$, $S_2$, $S_3$ act in the directions $(l_1', m_1', n_1')$, $(l_2', m_2', n_2')$ and $(l_3', m_3', n_3')$, and are referred, according to definition, to the unstrained elements of area upon which they act. Referred to elements of area as affected by strain, let the stresses be $\bar{S}_1$, $\bar{S}_2$, $\bar{S}_3$. Then

$$\bar{S}_1 = \frac{S_1}{(1+e_2)(1+e_3)}, \text{ etc.} \quad . \quad . \quad . \quad . \quad (8)$$

We write further, $\overline{rr}$, $\overline{\theta\theta}$, $\overline{zz}$, $\overline{\theta z}$, $\overline{zr}$, and $\overline{r\theta}$ for stresses

referred to the actual (strained) elements of area upon which they act, and referred also to $r, \theta, z$ axes at the point $\bar{r}, \bar{\theta}, \bar{z}$. Thus $\overline{rr}$, for instance, is the stress acting in the direction of the $r$ axis of $P_1$ upon an element of area at $P_1$ normal to this direction. These stresses, given in terms of $\bar{S}_1$, $\bar{S}_2$, and $\bar{S}_3$ by such equations as

$$\overline{rr} = \bar{S}_1 l_1'^2 + \bar{S}_2 l_2'^2 + \bar{S}_3 l_3'^2 \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and

$$\overline{\theta z} = \bar{S}_1 m_1' n_1' + \bar{S}_2 m_2' n_2' + \bar{S}_3 m_3' n_3' \quad . \quad (10)$$

must be expressed in terms of $u, v, w$.

We have

$$\frac{(1+\sigma)(1-2\sigma)}{E}\overline{rr} = \sum_{1,2,3} \frac{(1-2\sigma)e_1 + \sigma\Sigma e_1}{(1+e_2)(1+e_3)} l_1'^2$$

$$= \Sigma \frac{(1-2\sigma)e_1 + \sigma\Sigma e_1}{(1+e_1)^2(1+e_2)(1+e_3)} \left[ l_1\left(1+\frac{\partial u}{\partial r}\right) + n_1 \frac{\partial u}{\partial z}\right]^2, \quad (11)$$

using equation (5). $u$ is of order $\tau^2$, at greatest the extensions $e$ are of order $\tau$, while $\overline{rr}$ is only wanted to the order $\tau^2$. Hence the expression reduces immediately to

$$\Sigma \frac{(1-2\sigma)e_1 + \sigma\Sigma e_1}{(1+e_1)^2(1+e_2)(1+e_3)} l_1^2,$$

and further, on expansion, neglecting of course terms of the third order in the extensions, to

$$(1-2\sigma)\Sigma e_1 l_1^2 + \sigma\Sigma e_1 - (1-2\sigma)\Sigma e_1^2 l_1^2 - (1-\sigma)\Sigma e_1 \cdot \Sigma e_1 l_1^2 - \sigma(\Sigma e_1)^2.$$

Since $(1+e_1)^2$ is a stationary value of $(1+e)^2$, from (4)

$$Al_1 + Hm_1 + Gn_1 = (1+e_1)^2 l_1, \quad . \quad . \quad . \quad (12)$$

$$Hl_1 + Bm_1 + Fn_1 = (1+e_1)^2 m_1, \quad . \quad . \quad . \quad (13)$$

and

$$Gl_1 + Fm_1 + Cn_1 = (1+e_1)^2 n_1, \quad . \quad . \quad . \quad (14)$$

with two similar sets of equations with suffixes 2 and 3. These equations need only be used in the evaluation of terms of the first order: for the others we have the simpler equations

$$\frac{\partial u}{\partial r} l_1 + \frac{1}{2}\left(\frac{\partial v}{\partial r} - \frac{v}{r}\right) m_1 + \frac{1}{2}\left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial r}\right) n_1 = e_1 l_1, \quad (15)$$

$$\frac{1}{2}\left(\frac{\partial v}{\partial r} - \frac{v}{r}\right) l_1 + \frac{u}{r} m_1 + \frac{1}{2}\frac{\partial v}{\partial z} n_1 = e_1 m_1, \quad (16)$$

and

$$\frac{1}{2}\left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial r}\right) l_1 + \frac{1}{2}\frac{\partial v}{\partial z} m_1 + \frac{\partial w}{\partial z} n_1 = e_1 n_1. \quad (17)$$

From (12),

$$\Sigma(1+e_1)^2 l_1^2 = \mathrm{A}$$
$$= \left(1+\frac{\partial u}{\partial r}\right)^2 + \left(1+\frac{u}{r}\right)^2 \left(\frac{\partial v}{\partial r} - \frac{v}{r}\right)^2 + \left(\frac{\partial w}{\partial r}\right)^2$$
$$= 1 + 2\frac{\partial u}{\partial r},$$

since $u$, $\frac{\partial v}{\partial r} - \frac{v}{r}$, and $w$ are all of order $\tau^2$.

From (15),

$$\Sigma e_1^2 l_1^2 = \left(\frac{\partial u}{\partial r}\right)^2 + \frac{1}{4}\left(\frac{\partial v}{\partial r} - \frac{v}{r}\right)^2 + \frac{1}{4}\left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial r}\right)^2$$
$$= 0,$$

to order $\tau^2$. Hence

$$\Sigma e_1 l_1^2 = \frac{\partial u}{\partial r}, \quad \ldots\ldots \quad (18)$$

to the approximation needed.

Again,

$$\Sigma(1+e_1)^2 = \mathrm{A} + \mathrm{B} + \mathrm{C}$$
$$= 1 + 2\frac{\partial u}{\partial r} + 1 + \frac{2u}{r} + 1 + 2\frac{\partial w}{\partial z} + \left(\frac{\partial v}{\partial z}\right)^2,$$

while from equations (15), (16), and (17),

$$\Sigma e_1^2 = \left[\frac{\partial u}{\partial r} + \frac{u}{r} + \frac{\partial w}{\partial z}\right]^2$$
$$-2\left[\frac{u}{r}\cdot\frac{\partial w}{\partial z} + \frac{\partial w}{\partial z}\frac{\partial u}{\partial r} + \frac{\partial u}{\partial r}\frac{u}{r} - \frac{1}{4}\left(\frac{\partial v}{\partial z}\right)^2 - \frac{1}{4}\left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial r}\right)^2 - \frac{1}{4}\left(\frac{\partial v}{\partial r} - \frac{v}{r}\right)^2\right]$$
$$= \frac{1}{2}\left(\frac{\partial v}{\partial z}\right)^2,$$

approximately. Consequently

$$\Sigma e_1 = \frac{\partial u}{\partial r} + \frac{u}{r} + \frac{\partial w}{\partial z} + \frac{1}{4}\left(\frac{\partial v}{\partial z}\right)^2. \quad \ldots \quad (19)$$

(18) and (19) give $\Sigma e_1 l_1^2$ and $\Sigma e_1$ in terms of $u$, $v$, $w$ to the accuracy required ; the remaining terms in the expression for $\overline{rr}$ are of the second order, and do not require special consideration. The other stresses are evaluated in the same way.

Using equations (3), the final expressions are

$$\frac{(1+\sigma)(1-2\sigma)}{\mathrm{E}}\overline{rr}=(1-\sigma)\frac{\partial u'}{\partial r}+\sigma\left(\frac{u'}{r}+\frac{\partial w'}{\partial z}\right)+\frac{\sigma}{4}\tau^2r^2,$$

$$\frac{(1+\sigma)(1-2\sigma)}{\mathrm{E}}\overline{\theta\theta}=(1-\sigma)\frac{u'}{r}+\sigma\left(\frac{\partial u'}{\partial r}+\frac{\partial w'}{\partial z}\right)+\left(\frac{5}{8}-\sigma\right)\tau^2r^2,$$

$$\frac{(1+\sigma)(1-2\sigma)}{\mathrm{E}}\overline{zz}=(1-\sigma)\frac{\partial w'}{\partial z}+\sigma\left(\frac{\partial u'}{\partial r}+\frac{u'}{r}\right)+\frac{1}{8}\tau^2r^2,$$

$$\frac{2(1+\sigma)}{\mathrm{E}}\overline{\theta z}=\tau r+\frac{\partial v'}{\partial z},$$

$$\frac{2(1+\sigma)}{\mathrm{E}}\overline{zr}=\frac{\partial u'}{\partial z}+\frac{\partial w'}{\partial r},$$

and

$$\frac{2(1+\sigma)}{\mathrm{E}}\overline{r\theta}=\frac{\partial v'}{\partial r}-\frac{v'}{r}.$$

5. *The Stress Equations.*

The equations for the equilibrium of an elastic body under no body forces, referred to orthogonal curvilinear coordinates $\alpha$, $\beta$, $\gamma$, are *

$$\frac{\partial}{\partial\alpha}\frac{\widehat{\alpha\alpha}}{h_2h_3}+\frac{\partial}{\partial\beta}\frac{\widehat{\alpha\beta}}{h_3h_1}+\frac{\partial}{\partial\gamma}\frac{\widehat{\gamma\alpha}}{h_1h_2}+\frac{\widehat{\alpha\beta}}{h_3}\frac{\partial}{\partial\beta}\left(\frac{1}{h_1}\right)+\frac{\widehat{\gamma\alpha}}{h_2}\frac{\partial}{\partial\gamma}\left(\frac{1}{h_1}\right)-\frac{\widehat{\beta\beta}}{h_3}\frac{\partial}{\partial\alpha}\left(\frac{1}{h_2}\right)-\frac{\widehat{\gamma\gamma}}{h_2}\frac{\partial}{\partial\alpha}\left(\frac{1}{h_3}\right)=0, \quad . \quad (20)$$

and two similar equations which can be written down from symmetry. The definitions of $h_1$, $h_2$, $h_3$ are contained in the statement that $ds$, the element of length between two neighbouring points, is given by the equation

$$(ds)^2=(d\alpha/h_1)^2+(d\beta/h_2)^2+(d\gamma/h_3)^2. \quad . \quad . \quad (21)$$

Ordinarily these equations are applied to first order problems, but in form they are accurate to any order of approximation. For the purpose of the problem here considered, $h_1$, $h_2$, and $h_3$ must be replaced by the quantities that arise in a formula similar to (21), giving the distance after strain between two points that then have coordinates $\bar{r}$, $\bar{\theta}$, $\bar{z}$, and $\bar{r}+d\bar{r}$, $\bar{\theta}+d\bar{\theta}$, $\bar{z}+d\bar{z}$. Accordingly

$$h_1=h_3=1, \quad 1/h_2=r+u.$$

Further, the stresses $\widehat{\alpha\alpha}$, ..., must be replaced by $\overline{rr}$, ...,

* Love, *loc. cit.*, § 58.

and $\partial/\partial\alpha$, $\partial/\partial\beta$, $\partial/\partial\gamma$, by $\partial/\partial\bar{r}$, $\partial/\partial\bar{\theta}$, $\partial/\partial\bar{z}$. With these substitutions the stress equations (20) become

$$\frac{\partial}{\partial\bar{r}}\{(r+u)\overline{rr}\}+\frac{\partial r\overline{\theta}}{\partial\bar{\theta}}+\frac{\partial}{\partial\bar{z}}\{(r+u)\overline{zr}\}$$

$$-\overline{\theta\theta}\frac{\partial}{\partial\bar{r}}(r+u)=0, \quad . \quad . \quad (22)$$

$$\frac{\partial}{\partial\bar{r}}\{(r+u)\overline{r\theta}\}+\frac{\partial\theta\overline{\theta}}{\partial\bar{\theta}}+\frac{\partial}{\partial z}\{(r+u)\overline{\theta z}\}$$

$$+\overline{r\theta}\frac{\partial}{\partial\bar{r}}(r+u)+\overline{\theta z}\frac{\partial}{\partial\bar{z}}(r+u)=0, \quad . \quad . \quad (23)$$

and

$$\frac{\partial}{\partial\bar{r}}\{r+u)\overline{zr}\}+\frac{\partial\overline{\theta z}}{\partial\bar{\theta}}+\frac{\partial}{\partial\bar{z}}\{(r+u)\overline{zz}\}$$

$$-\overline{\theta\theta}\frac{\partial}{\partial\bar{z}}(r+u)=0. \quad . \quad . \quad (24)$$

To the first order of $u$, $v$, $w$,

$$\frac{\partial}{\partial\bar{r}}=\left(1-\frac{\partial u}{\partial r}\right)\frac{\partial}{\partial r}-\left(\frac{\partial v}{r\partial r}-\frac{v}{r^2}\right)\frac{\partial}{\partial\theta}-\frac{\partial w}{\partial r}\frac{\partial}{\partial z},$$

$$\frac{\partial}{\partial\bar{\theta}}=-\frac{\partial u}{\partial\theta}\frac{\partial}{\partial r}+\left(1-\frac{\partial v}{r\partial\theta}\right)\frac{\partial}{\partial\theta}-\frac{\partial w}{\partial\theta}\frac{\partial}{\partial z},$$

and

$$\frac{\partial}{\partial\bar{z}}=-\frac{\partial u}{\partial z}\frac{\partial}{\partial r}-\frac{1}{r}\frac{\partial v}{\partial z}\frac{\partial}{\partial\theta}+\left(1-\frac{\partial w}{\partial z}\right)\frac{\partial}{\partial z},$$

in the general case, while here, as all quantities are independent of $\theta$,

$$\frac{\partial}{\partial\bar{r}}=\left(1-\frac{\partial u}{\partial r}\right)\frac{\partial}{\partial r}-\frac{\partial w}{\partial r}\frac{\partial}{\partial z}, \quad \frac{\partial}{\partial\bar{\theta}}=0,$$

and

$$\frac{\partial}{\partial\bar{z}}=-\frac{\partial u}{\partial z}\frac{\partial}{\partial r}+\left(1-\frac{\partial w}{\partial z}\right)\frac{\partial}{\partial z}.$$

Consequently $\partial/\partial\bar{r}$ differs from $\partial/\partial r$ by a quantity of order $\tau^2$, as does $\partial/\partial\bar{z}$ from $\partial/\partial z$. Moreover, in equations (22), (23), and (24), $r+u$ differs from $r$ by a quantity of order $\tau^2$, while the stresses are at greatest of order $\tau$. To the order $\tau^2$ then, the equations are

$$\frac{\partial\overline{rr}}{\partial r}+\frac{\partial\overline{zr}}{\partial z}+\frac{\overline{rr}-\overline{\theta\theta}}{r}=0, \quad . \quad . \quad . \quad . \quad (25)$$

$$\frac{\partial\overline{r\theta}}{\partial r}+\frac{\partial\overline{\theta z}}{\partial z}+\frac{2\overline{r\theta}}{r}=0, \quad . \quad . \quad . \quad . \quad . \quad (26)$$

and

$$\frac{\partial\overline{zr}}{\partial r}+\frac{\partial\overline{zz}}{\partial z}+\frac{\overline{zr}}{r}=0. \quad . \quad . \quad . \quad . \quad . \quad (27)$$

As these are the stress equations of the ordinary theory, it follows that the precise interpretations that have been placed on the symbols in equation (20) are really unnecessary, but it does not appear possible to show this without the formal statement that has been made.

6. Substituting the expressions of § 4 for the stresses, we have the equations

$$(1-\sigma)\left(\frac{\partial^2 u'}{\partial r^2}+\frac{1}{r}\frac{\partial u'}{\partial r}-\frac{u'}{r^2}\right)+\frac{1-2\sigma}{2}\frac{\partial^2 u'}{\partial z^2}+\frac{1}{2}\frac{\partial^2 w'}{\partial z \partial r}+\frac{14\sigma-5}{8}\tau^2 r=0, \quad . \quad . \quad (28)$$

$$\frac{\partial^2 v'}{\partial r^2}+\frac{1}{r}\frac{\partial v'}{\partial r}-\frac{v'}{r^2}+\frac{\partial^2 v'}{\partial z^2}=0, \quad . \quad . \quad (29)$$

and

$$\frac{1}{2}\left(\frac{\partial^2 u'}{\partial z \partial r}+\frac{1}{r}\frac{\partial u'}{\partial z}\right)+(1-\sigma)\frac{\partial^2 w'}{\partial z^2}+\frac{1-2\sigma}{2}\left(\frac{\partial^2 w'}{\partial r^2}+\frac{1}{r}\frac{\partial w'}{\partial r}\right)=0. \quad . \quad . \quad (30)$$

### 7. *The Boundary Conditions.*

To complete the solution the boundary conditions must now be obtained. The surface, $r=a$, of the cylinder is supposed free from external force. The corresponding conditions need not be considered in detail *: they reduce simply to

$$\overline{rr}=\overline{r\theta}=\overline{zr}=0, \quad r=a,$$

or, written in full,

$$(1-\sigma)\frac{\partial u'}{\partial r}+\sigma\left(\frac{u'}{r}+\frac{\partial w'}{\partial z}\right)+\frac{\sigma}{4}\tau^2 r^2=0, \quad . \quad . \quad (31)$$

$$\frac{\partial v'}{\partial r}-\frac{v'}{r}=0, \quad . \quad . \quad (32)$$

and

$$\frac{\partial u'}{\partial z}+\frac{\partial w'}{\partial r}=0, \quad . \quad . \quad (33)$$

when $r=a$.

* General formulæ from which the conditions in this particular case can be written down are given in the paper quoted above, Proc. Roy. Soc. A, vol. cvii. p. 742.

### 8. *The First Solution.*

Equations (29) and (32) are satisfied by $v'=0$. Writing further

$$u'=f(r), \quad w'=\beta z,$$

where $\beta$ is a constant, equations (30) and (33) are satisfied, and (28) becomes

$$r^2f''(r)+rf'(r)-f(r)=\frac{5-14\sigma}{8(1-\sigma)}\tau^2r^3.$$

The solution is

$$f(r)=\alpha r+\gamma/r+\frac{5-14\sigma}{64(1-\sigma)}\tau^2r^3,$$

where $\alpha$ and $\gamma$ are constants, of which $\gamma$ must evidently be zero. So that

$$u'=\alpha r+\frac{5-14\sigma}{64(1-\sigma)}\tau^2r^3, \quad . \quad . \quad . \quad . \quad (34)$$

and $$w'=\beta z,$$

while from (31) we must have

$$\alpha+\sigma\beta=-\frac{3(1-2\sigma)(5-2\sigma)}{64(1-\sigma)}\tau^2a^2.$$

The original displacements (1) refer of course only to the case in which the cylinder is strained by twisting couples alone; the one other relation needed to complete the determination of $\alpha$ and $\beta$ must therefore come from the condition that there must be no tensional stress on the cylinder. Actually this condition is

$$\int_0^a\left(1+\frac{u'}{r}\right)\left(1+\frac{\partial u'}{\partial r}\right)\bar{zz}\,r\,dr=0,$$

since $\bar{zz}$ is by definition referred to the strained element of area, but to find $\alpha$ and $\beta$ to the order $\tau^2$, this may be replaced by

$$\int_0^a\bar{zz}\,r\,dr=0.$$

Substituting for $\bar{zz}$,

$$\int_0^a\left[(1-\sigma)\beta+2\sigma\alpha+\left\{\frac{1}{8}+\frac{\sigma(5-14\sigma)}{16(1-\sigma)}\right\}\tau^2r^2\right]r\,dr=0,$$

whence $$(1-\sigma)\beta+2\sigma\alpha=-\frac{(1-2\sigma)(2+7\sigma)}{32(1-\sigma)}\tau^2a^2.$$

Finally then

$$\alpha = -\frac{15-25\sigma-8\sigma^2}{64(1-\sigma^2)}\tau^2a^2, \quad . \quad . \quad . \quad . \quad (35)$$

and

$$\beta = -\frac{1-3\sigma}{16(1+\sigma)}\tau^2a^2. \quad . \quad . \quad . \quad . \quad . \quad (36)$$

$\beta$ of course measures the increase in the length of the wire per unit length, while from (34) and the value of $\alpha$ given by (35) we have the increase in radius in the form

$$\frac{u'}{a} = -\frac{5-3\sigma}{32(1+\sigma)}\tau^2a^2. \quad . \quad . \quad . \quad . \quad (37)$$

### 9. *The Effect of Tension.*

The solution given applies to the case in which the cylinder is unstressed initially, whereas the experimental work was done on wires in tension due to loads that were in most cases considerable. It is easy to extend the analysis to see whether or not the secondary effects of twisting can be altered by subjecting the cylinder to tension.

The appropriate first order solution is given by

$$u = -\sigma \mathrm{A}r, \quad v = \tau rz, \quad w = \mathrm{A}z,$$

where A is constant * ; the second order solution by

$$u = -\sigma \mathrm{A}r + u', \quad v = \tau rz + v', \quad w = \mathrm{A}z + w'.$$

The method of the preceding paragraphs is quite general, and is adequate to find $u'$, $v'$, $w'$ to the second order of A and $\tau$. It has been verified that to this order $u'$, $v'$, and $w'$ are not altered by A, so that (36) and (37) give the *additional* elongation and *additional* alteration in radius due to a twist of amount $\tau$ in a wire with any load. A different result indeed could hardly have been expected. It has not therefore appeared necessary to give the work in the general case in detail.

### 10. *Comparison with Experiment.*

Poynting's experimental work † on the changes in dimensions of a twisted wire was undertaken to test his view that an elastic body could not be held in a state of simple shear by shearing forces only, but that in particular a pressure

* The tension in the cylinder is therefore supposed uniform. That in a loaded wire is, of course, only approximately uniform owing to the weight of the wire, but any alteration this may cause in the secondary effects cannot be appreciable.

† Proc. Roy. Soc. A, vol. lxxxii. p. 546, and Proc. Roy. Soc. A, vol. lxxxvi. p. 534; or 'Collected Scientific Papers,' Arts. 25 and 30.

(or tension) perpendicular to the planes of shear would be required. On the theory of elasticity only a shearing force is necessary to maintain this strain; a pressure of this type must be entirely a second-order effect. Such a stress implies a similar one with transverse waves, and it was with the problem of wave motion that Poynting was fundamentally concerned. That there would be a pressure in this case was suggested by the existence of the pressures of light and of sound waves. Returning to the statical problem, a body acted upon by shearing forces only will, if the secondary pressure due to shear exists, elongate in a direction perpendicular to the planes of shear, while similar secondary alterations will take place in the dimensions of a twisted wire. In the latter case alterations were detected and measured by Poynting.

Only in one respect is there any agreement between these measurements and those predicted by equations (36) and (37). It is sufficient to quote the experimental results for the alteration in length of a wire due to twisting given in the following table. A steel piano-wire, 230 cm. long and of diameter 0·072 cm., was loaded and held at one end, while the other was twisted through eight complete turns *.

Table I.

| Load (grammes). | Lowering (mm.) of end point. |
|---|---|
| 1081 | −0·139 |
| 3081 | +0·0498 |
| 5081 | +0·0660 |
| 7081 | +0·0732 |
| 9081 | +0·0749 |

Consequently, with a small load a shortening of the wire was found, but on increasing the load this changed to a lengthening which finally approached a value not altered to any extent by further increase of load. The shortening was attributed by Poynting to the original coiled configuration of the wire, and the final value of the lengthening was accepted as measuring the real secondary effect of the twist.

* These results are taken from 'Scientific Papers,' Art. 25, pp. 365, 368. That the alteration (whether in length or in diameter) was approximately proportional to the square of the twist was verified in all cases. Here therefore, as elsewhere, the results for one twist only are given.

The present theory gives an alteration that, at any rate to the limits of accuracy of these measurements, is independent of the load, and which from (36) is a shortening, provided $\sigma$ is less than 1/3. For the wire used in the experiment, the following values of the elastic constants were found:

$$E = 2{\cdot}013 \times 10^{12}, \quad \mu = 0{\cdot}769 \times 10^{12}.$$

The value of $\sigma$ is then 0·309. A shortening is therefore predicted, which, as $\sigma$ is so near 1/3, is exceedingly small. The value of $\tau a$ may be determined from

$$230\ \tau a = 16\pi a = 16\pi(\cdot 036);$$

using (36) the rise of the end point is found to be $5 \times 10^{-4}$ mm. The theory then predicts in this case an alteration in length too small to have been measured, and since $\sigma$ is usually in the neighbourhood of 1/3, it will agree no better with the other experiments.

Where changes in diameter are concerned the theory is not so seriously at fault. In every experiment it was found that the diameter of the wire decreased on twisting, and evidently the theoretical value of $u'/a$ is always negative. The following table gives observed values of $u'/a$ * and those calculated from (37) for one complete turn of the end point of the wire. The lengths of the three wires were the same, 160·5 cm.

Table II.

| Wire. | Diameter (cm.). | $\sigma$. | $-u'/a$ obs. | $-u'/a$ calc. |
|---|---|---|---|---|
| Steel I. ..... | ·0986 | ·27 | $3{\cdot}19 \times 10^{-7}$ | $3{\cdot}8 \times 10^{-7}$ |
| Steel II..... | ·1210 | ·27 | $5{\cdot}24 \times 10^{-7}$ | $5{\cdot}8 \times 10^{-7}$ |
| Copper ..... | ·1219 | ·33 | $1{\cdot}75 \times 10^{-6}$ | $5{\cdot}4 \times 10^{-7}$ |

The theory then gives a good result with the steel wires, and one at least of the right order of magnitude in the case of the copper wire †.

It may be mentioned that before these experiments the wires were straightened by passing electric currents through

* 'Scientific Papers,' Art. 30, pp. 410, 411. Actually these values of $u'/a$ are mean values, results from experiments with various twists being correlated by assuming the square law. It was found throughout that the alterations depended on the direction (whether clockwise or counter-clockwise) of the twist. The effect of this may be supposed eliminated in the mean values; it is in any case beyond the scope of the present work. A theory is suggested by Poynting, *loc. cit.* p. 420.

† The experiments on the copper wire were not so comprehensive as those on the steel wires, and the same weight was not attached to the results.

them while loaded. After this treatment the secondary effects were found to be roughly independent of the load, though in the first instance shortening with light loads had been observed as in the experiments quoted in Table I.

### 11. *The Second Solution.*

Better, though still not satisfactory, agreement with experiment can be obtained by modifying the fundamental assumption upon which the preceding work has been based. The assumption of §2 is altered merely in defining stress as the action over an element of surface divided by the area of the surface *after* strain. Equations (2) and the definition of extension remain the same. That part of the preceding work which relates to the expression of functions of the principal extensions in terms of $u$, $v$, and $w$ remains unchanged. The only differences are in the expressions for the stress components $\overline{rr}$, . . . . (defined as before) in terms of $e_1$, $e_2$, $e_3$. Evidently

$$\frac{(1+\sigma)(1-2\sigma)}{E}\overline{rr} = \sum_{1,2,3}[(1-2\sigma)e_1 + \sigma\Sigma e_1]l_1'^2$$

$$= \Sigma\frac{(1-2\sigma)e_1 + \sigma\Sigma e_1}{(1+e_1)^2}\left[l_1\left(1+\frac{\partial u}{\partial r}\right) + n_1\frac{\partial u}{\partial z}\right]^2.$$

Since $u$ is of order $\tau^2$ this is, to our approximation,

$$\Sigma\frac{(1-2\sigma)e_1 + \sigma\Sigma e_1}{(1+e_1)^2}l_1^2$$

or $\quad (1-2\sigma)\Sigma e_1 l_1^2 + \sigma\Sigma e_1 - 2(1-2\sigma)\Sigma e_1^2 l_1^2 - 2\sigma\Sigma e_1 \cdot \Sigma e_1 l_1^2.$

Equations (18) and (19) are applicable as before, and the stresses can be immediately expressed in terms of $u$, $v$, $w$. The results are

$$\frac{(1+\sigma)(1-2\sigma)}{E}\overline{rr} = (1-\sigma)\frac{\partial u'}{\partial r} + \sigma\left(\frac{u'}{r} + \frac{\partial w'}{\partial z}\right) + \frac{\sigma}{4}\tau^2\gamma^2,$$

$$\frac{(1+\sigma)(1-2\sigma)}{E}\overline{\theta\theta} = (1-\sigma)\frac{u'}{r} + \sigma\left(\frac{\partial u'}{\partial r} + \frac{\partial w'}{\partial z}\right) + \left(\frac{3}{8} - \frac{\sigma}{2}\right)\tau^2\gamma^2,$$

$$\frac{(1+\sigma)(1-2\sigma)}{E}\overline{zz} = (1-\sigma)\frac{\partial w'}{\partial z} + \sigma\left(\frac{\partial u'}{\partial r} + \frac{u'}{r}\right) - \left(\frac{1}{8} - \frac{\sigma}{2}\right)\tau^2\gamma^2,$$

$$\frac{2(1+\sigma)}{E}\overline{\theta z} = \tau r + \frac{\partial v'}{\partial z},$$

$$\frac{2(1+\sigma)}{E}\overline{zr} = \frac{\partial u'}{\partial z} + \frac{\partial w'}{\partial r},$$

and $\quad \frac{2(1+\sigma)}{E}\overline{r\theta} = \frac{\partial v'}{\partial r} - \frac{v'}{r}.$

The stress equations (25), (26), and (27) are unchanged, whence the equations

$$(1-\sigma)\left(\frac{\partial^2 u'}{\partial r^2}+\frac{1}{r}\frac{\partial u'}{\partial r}-\frac{u'}{r^2}\right)+\frac{1-2\sigma}{2}\frac{\partial^2 u'}{\partial z^2}+\frac{1}{2}\frac{\partial^2 w'}{\partial z\partial r}$$
$$+\left(\frac{5\sigma}{4}-\frac{3}{8}\right)\tau^2 r=0,$$

$$\frac{\partial^2 v'}{\partial r^2}+\frac{1}{r}\frac{\partial v'}{\partial r}-\frac{v'}{r^2}+\frac{\partial^2 v'}{\partial z^2}=0,$$

and

$$\frac{1}{2}\left(\frac{\partial^2 u'}{\partial z\partial r}+\frac{1}{r}\frac{\partial u'}{\partial z}\right)+(1-\sigma)\frac{\partial^2 w'}{\partial z^2}+\frac{1-2\sigma}{2}\left(\frac{\partial^2 w'}{\partial r^2}+\frac{1}{r}\frac{\partial w'}{\partial r}\right)=0.$$

The boundary conditions are

$$\overline{rr}=\overline{r\theta}=\overline{zr}=0, \quad r=a.$$

Setting $u'=f(r), \quad v'=0, \quad w'=\beta z,$

$\beta$ constant, we have the single equation

$$f''(r)+\frac{1}{r}f'(r)-\frac{1}{r^2}f(r)-\frac{3-10\sigma}{8(1-\sigma)}\tau^2 r=0,$$

and the single condition

$$(1-\sigma)f'(r)+\sigma\{f(r)/r+\beta\}+\frac{\sigma}{4}\tau^2 r^2=0, \quad r=a.$$

Consequently

$$u'=\alpha r+\frac{3-10\sigma}{64(1-\sigma)}\tau^2 r^3,$$

where $$\alpha+\sigma\beta+\tau^2 a^2\left[\frac{\sigma}{4}+\frac{(3-2\sigma)(3-10\sigma)}{64(1-\sigma)}\right]=0. \quad . \quad (38)$$

Finally, there is the condition that the cylinder is not in tension,

$$\int_0^a\left(1+\frac{u'}{r}\right)\left(1+\frac{\partial u'}{\partial r}\right)\overline{zz}\,r\,dr=0,$$

or, accurately enough,

$$\int_0^a \overline{zz}\,r\,dr=0.$$

Substituting for $\overline{zz}$,

$$\int_0^a\left[(1-\sigma)\beta+2\sigma\alpha+\tau^2 r^2\left\{\frac{\sigma}{2}-\frac{1}{8}+\frac{4\sigma(3-10\sigma)}{64(1-\sigma)}\right\}\right]r\,dr=0,$$

whence

$$(1-\sigma)\beta+2\sigma\alpha+\frac{\tau^2 a^2}{2}\left[\frac{\sigma}{2}-\frac{1}{8}+\frac{\sigma(3-10\sigma)}{16(1-\sigma)}\right]=0. \quad (39)$$

From (38) and (39) we have the simple result

$$\beta = \tau^2 a^2/16, \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

giving the alteration in length, while

$$\alpha = -\frac{9-16\sigma}{64(1-\sigma)},$$

so that the alteration in radius is given by

$$u'/a = -3\tau^2 a^2/32. \quad . \quad . \quad . \quad . \quad . \quad (41)$$

## 12. *Comparison with Experiment.*

On this theory a twisted wire always lengthens; the increase per unit length and the fractional decrease in radius are both, for given twist and given radius, independent of the material, and the first ratio is two-thirds of the other. The following table compares these results with those of the experiments quoted in Table II.

Table III.

| Wire. | Diam. (cm.). | $\beta$ obs. | $\beta$ calc. | $-u'/a$ obs. | $-u'/a$ calc. |
|---|---|---|---|---|---|
| Steel I. ... | ·0986 | $1{\cdot}71\times10^{-6}$ | $2{\cdot}3\times10^{-7}$ | $3{\cdot}19\times10^{-7}$ | $3{\cdot}5\times10^{-7}$ |
| Steel II.... | ·1210 | $2{\cdot}90\times10^{-6}$ | $3{\cdot}5\times10^{-7}$ | $5{\cdot}24\times10^{-7}$ | $5{\cdot}3\times10^{-7}$ |
| Copper ... | ·1219 | $4{\cdot}25\times10^{-6}$ | $3{\cdot}6\times10^{-7}$ | $1{\cdot}75\times10^{-6}$ | $5{\cdot}3\times10^{-7}$ |

As regards the alteration in length the agreement is still unsatisfactory: the theory now gives a lengthening, and to that extent is an improvement on the previous theory, but one only about one-tenth of the experimental value. Both theories give roughly the same alteration in radius.

As before it can be shown to be the case that the effect on the theoretical results of supposing the wire to be loaded is negligible.

## 13. *Conclusion.*

The consistency of the results of Poynting's two series of experiments makes it almost certain that the real alteration in length due to twist is the lengthening found with wires with large loads. The effects of overstrain, whether by twisting or by loading, were avoided. The circumstance that the alterations depended on the direction of the twist implies that there was internal strain, and the possibility that this

may have affected the results exists. But it is reasonable to suppose that the mean values quoted above are, if not independent of this strain, at least not greatly affected by it. Poynting has shown * that on a simple hypothesis as to the cause of the internal strain, the mean values are independent of its magnitude. In any case using either of the assumptions as to the relations between stress and strain, and assuming any internal strain that will cause asymmetry, it would appear quite impossible to obtain anything other than a fractional alteration in the previous theoretical results for lengthening. The result of the first theory is practically that there is no alteration in length, while the second gives a lengthening only about one-tenth of that found experimentally. In this respect then there is definite disagreement with experiment. It cannot be said with such certainty, if at all, that the theories fail to account for the accompanying alteration in radius, as in the only experiments to which importance was attached the values are in close agreement with those predicted by either theory. However, the experimental difficulties of measuring the alteration in radius probably make the other measurement the more reliable.

It is only possible to conclude that neither extension of Hooke's law is in accordance with the actual behaviour of elastic bodies, and those given are the only satisfactory ones that can be made without introducing new elastic constants. It is certainly possible, for instance, to define extension in a different way as the ratio of the increase in length of an element to its length after strain ; then, with the two definitions of stress already used, two other statements of Hooke's law with only the two usual elastic constants can be obtained from equations (2). But these are practically the only other possibilities, and the definition of extension upon which they rest is not a natural or a satisfactory one. Any other theories require terms of the second order in the extensions in the equations (2) giving the stresses, and consequently new elastic constants. Poynting's experiments are probably not comprehensive enough to determine these.

* *Loc. cit.* p. 421.

CXX. *The J Phenomenon in X-Rays.*—Part II. *Application to Scattered X-Rays.* *By* C. G. Barkla, *F.R.S.*, *and* S. R. Khastgir, *Ph.D.*, *University of Edinburgh* *.

*Introduction.*

THE recent publication † of a preliminary account of the J phenomenon in X-rays enables us to give an intelligible account of many phenomena associated with scattered X-rays. Such phenomena have recently received a great deal of attention, partly because the well-known difference sometimes appearing between primary and scattered X-rays has been observed by the X-ray spectrometer, and partly because of the daring hypothesis put forward by A. H. Compton to explain these experimental results.

Before discussing this work it is not inappropriate to say a few words on our experimental methods. There are very many advantages in identifying X-radiation by its penetrating power or, by what is more convenient to express, its absorbability. In investigating fundamental phenomena the method seems in many respects immensely superior to the spectroscopic method—indeed, the absorption method becomes a necessity, for in certain regions wave-length fails to define a radiation; absorbability becomes more fundamental.

The following advantages of the absorption method may be noticed :—

(1) Great accuracy may be obtained in the detection and measurement, not of the absorption-coefficients themselves, but of differences or changes of absorption-coefficients. Indeed, it appears that much higher accuracy can be obtained than by the spectroscopic measurements.

(2) The absorption experiments are much simpler, and, as the results will show, are probably much less liable to misinterpretation.

(3) The processes taking place are capable of detailed examination; the whole apparatus may be easily modified and the important parts be dissected so that changes in the scattering substance, in the absorbing substance, and in the detecting apparatus may be studied in detail. This is not possible with the X-ray spectrometer, for with this comparatively huge masses of scattering substance must be used, and the radiation must pass through thick layers of crystal

* Communicated by the Authors.
† Barkla, Phil. Mag. May 1925.

before its effect can be observed. Transmission through matter is assumed to affect only the intensity.

(4) In the absorption method the experimental conditions may be so varied and the results may be obtained so rapidly, that the ground covered is enormous in comparison with that possible with the X-ray spectrometer. (It is doubtful if the results already obtained upon the J phenomenon could have been obtained in a century's work with the spectrometer.)

(5) The absorption method, too, gives the results of experiments of short duration ; whereas in many cases the results of spectroscopic work are simply the average over long periods during which changes may have, and as we shall show probably have, occurred.

(6) By the absorption method, effects may be observed which could never be detected by the X-ray spectrometer because, as we have found, X-ray phenomena are not governed by mere wave-length. In fact, for the investigation of such new phenomena few instruments could be more unsuitable than the X-ray spectroscope. It fetters the observer experimentally ; its use assumes much. New and fundamental facts must still be discovered by simple and somewhat primitive methods. Some of the finer developments may come later from spectroscopic observations. Our purpose in this paper is to show that the phenomena appearing in the investigation of scattered X-radiation are merely instances of the much more general J phenomenon, and to give further information regarding this phenomenon before proceeding to a consideration of its nature and meaning.

*Direct Comparison of Primary and Scattered Radiations.*

A series of measurements of the absorption coefficients of primary and of secondary X-radiations—the latter emitted by paper—was made by Barkla and Mrs. Sale *. These showed very definitely that when soft (low frequency) primary radiations were used the scattered radiation was, within the limits of experimental error, like the primary. There certainly was not a difference in absorption-coefficient of as much as 3 per cent. or in wave-length of 1 per cent. between the two radiations. (Compton's hypothetical difference would range from 3 to 5 per cent. in wave-length.) As the wave-length of primary radiation was reduced, there suddenly appeared—that is at a certain critical

* Phil. Mag. April 1923.

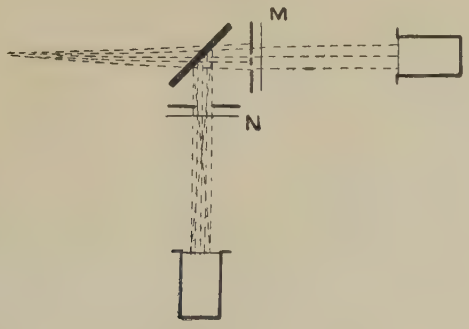
absorption-coefficient—a large difference between the secondary and the primary as usually measured. The secondary radiation abruptly became "softer" than the primary, and the percentage difference became more marked as the wave-length was reduced. It was pointed out at the time that this sudden appearance of a change in the absorption-coefficient of the scattered radiation might be accounted for by the J phenomenon. This has been fully confirmed by more recent experiments. The direct measurements of Barkla and Sale have been repeated and verified, but our results by this method add nothing to those given in their paper. Much greater accuracy, however, has since been obtained, not by measuring the absorption-coefficients of both primary and secondary beams and then comparing these, but by observing more directly any *difference* which may appear between the primary and secondary radiations, as the following description will show.

*Difference between Primary and Scattered Radiation.*

The method adopted, which proved to be very accurate and yielded some of the most instructive results, was as follows :—

The ratio of the ionizations produced in two similar electroscopes (see fig. 1), one by the secondary radiation from paper

Fig. 1.




proceeding in a direction at right angles to the primary, and the other by the primary beam or, rather, by fine pencils of the primary radiation, from various portions of the primary beam, was obtained. This ratio $\frac{\text{"secondary ionization"}}{\text{"primary ionization"}}$, or $\frac{S}{P}$, was usually very constant, the variations amounting to only about 1 per cent. Similar absorbing sheets of aluminium

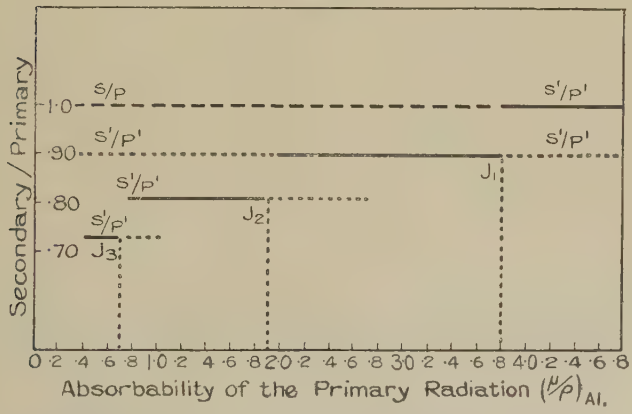
or other substance were placed at M and N in the paths of these two beams on their way to the electroscopes, and the ratio of ionizations was again determined: call it S′/P′. An unchanged ratio of course indicated equal absorptions of secondary and primary radiations; a fall in the ratio indicated that the secondary was the more absorbable. What was observed was either an exact equality or a well-marked difference between the two; *i.e.*, S′/P′ was either equal to or markedly less than S/P. The change from equality to inequality, which was produced by various means, was very abrupt; it was found to be marked by the J discontinuity as observed in other experiments (see Phil. Mag. May 1925).

The ratio S′/P′ of course depended upon the thickness of the absorbing sheets, but the greatest sensitivity and accuracy were obtained by using a thickness which diminished the ionization by about 50 per cent. A difference between S/P and S′/P′ of 1 per cent. would indicate a difference of absorption-coefficients of secondary and primary of about 1·4 per cent. corresponding to a difference of wave-length of less than 0·5 per cent. In any one experiment, however, it is important to notice the thickness of intercepting sheets was kept constant throughout the whole range of radiations experimented upon. The results of a very large number of experiments of this kind are all represented by fig. 2, in which the ratio of ionizations produced by the secondary and primary beams after transmission through fixed absorbing sheets (viz. S′/P′) is plotted for various radiations against the absorption-coefficient ($\mu/\rho$) of each radiation, this being measured from a 50 per cent. absorption as though the radiation were perfectly homogeneous.

The ratio S/P, that is the ratio of the ionizations produced by the *unintercepted* secondary and primary beams, was a constant throughout a long range of wave-lengths; this is shown by the highest horizontal broken line in the figure. (Barkla and Sale had obtained a slight fall of ratio with increase of frequency; but the constancy obtained throughout the experiments here described, when care was taken to eliminate stray radiations, was so marked that we cannot but regard this as expressing the truth, and the small slope obtained previously as being possibly not due to a primary action at all. Be that as it may, the constancy of ratio is the feature to be emphasized; deviations from that, though quite real in the particular experiments referred to, are, as an expression of fundamental actions, suspect; and in any case they are small.)

The constancy might of course be due to a balance of two opposing variations, an increase in the frequency of the primary being accompanied by diminished intensity of secondary radiation combined with increased absorbability and ionizing power compared with the primary. *A priori* such a balance is improbable; the constancy is so marked that it indicates not an approximate balance, but rather a definite absence of variation of either. However, the point is settled without any ambiguity by the results of the experiments, in which both primary and secondary beams were intercepted by absorbing sheets.

Fig. 2.




Broken line - - - - - - - is "unintercepted ratio" S/P.
Continuous line ——— is "intercepted ratio" S′/P′.
Dotted line ..... is occasional "intercepted ratio" S′/P′.

The ratio S′/P′—that is, the corresponding ratio obtained when both secondary and primary beams were transmitted through constant equal thicknesses of aluminium (say)—was either precisely the same as S/P or very widely different. Two cases must, however, be described, for all the results obtained throughout a very extensive series of experiments with apparatus of various forms, various X-ray tubes, various ionization chambers, etc., are all included in these two cases, *a* and *b*. These, then, are alternative results, either of which may appear; but the controlling condition has not yet been identified. It seems that the two apparently different results are really fundamentally governed by the same laws. Both are described below and are illustrated graphically in fig. 2. Briefly they are (*a*)—equality of absorption

coefficients of primary and secondary over a long range of low frequencies, with well marked differences appearing abruptly at higher frequencies; (*b*)—a constant difference of absorption coefficients of primary and secondary throughout the whole range of frequencies, with no discontinuity over this range.

Case *a*.

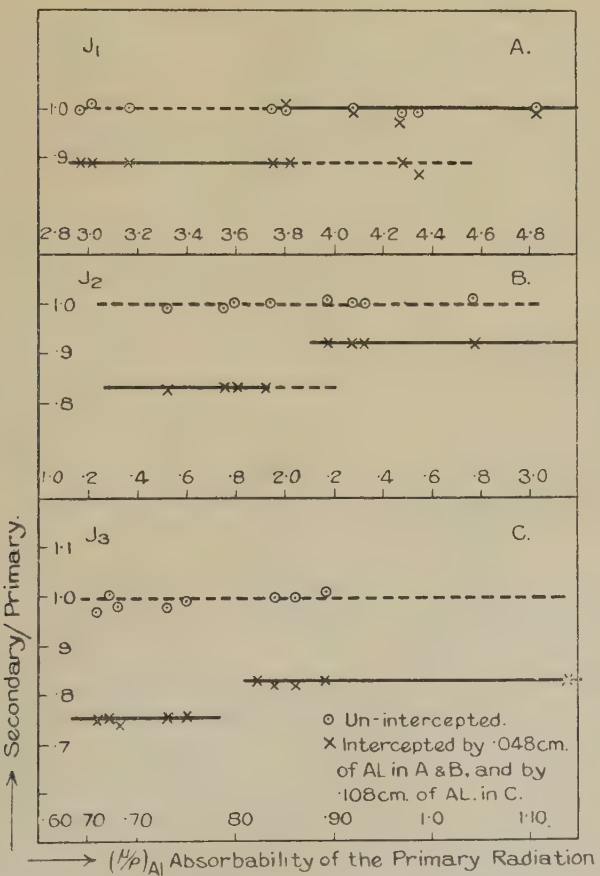
Beginning with soft radiation for which $\left(\frac{\mu}{\rho}\right)_{Al} = 10$ (say), or the wave-length is about ·8 Å.U. and gradually increasing the frequency, that is moving from right to left of fig. 2, the ratio $S'/P' = S/P$ very exactly, and it remains so as the frequency of radiation increases; *i. e.*, the continuous line at the highest level ($S'/P'$) coincides with the broken line for S/P. In this case (*a*) there is not the least indication of a difference until $\left(\frac{\mu}{\rho}\right)_{Al} = 3{\cdot}8$ approximately when the ratio $S'/P'$ suddenly drops say 10 * per cent below S/P; that is, when the penetrating power of the primary exceeds the critical value given by $\left(\frac{\mu}{\rho}\right)_{Al} = 3{\cdot}8$ approximately, a difference between the secondary and the primary suddenly appears. As the frequency is increased, this ratio $S'/P'$ again remains constant until a second critical absorbability is reached. When $\left(\frac{\mu}{\rho}\right)_{Al} = 1{\cdot}9$ approximately, a further drop in ratio $S'/P'$ occurs, and for higher-frequency radiations this ratio again remains constant until a third critical point is reached, $\left(\frac{\mu}{\rho}\right)_{Al} = 0{\cdot}7$, when there is a further drop of ratio $S'/P'$. Thus, while there is equality of penetrating powers of secondary and primary for soft radiations, there appear these sudden changes in the penetrating power of a secondary beam (as usually measured) at these critical absorbabilities, and when the primary radiation is of short wave-length, the difference between primary and secondary becomes very great indeed.

The values of the ratio $S'/P'$ all fall upon four continuous horizontal lines, the three steps from one level to another being marked $J_1$, $J_2$, $J_3$. Proceeding from low to high

* The precise amount depends on the thickness of aluminium used to intercept both beams; 10 per cent. is approximately the value for a thickness ·05 cm.

frequencies, that is moving from right to left of fig. 2, very occasional values were obtained at the lower level before the J discontinuity was definitely reached. These are shown by dotted lines to the right of the continuous lines *. Examples of the actual observations showing the three discontinuities are given in fig. 3. In this the circles represent "unintercepted

Fig. 3.




ratios" S/P; the crosses give the corresponding "intercepted ratios" S′/P′. Two of the lower occasional values for S′/P′ are shown before the $J_1$ discontinuity definitely occurred.

* The highest continuous line S′/P′ as shown on the figure is only a very small portion of a long line of observations showing equality of S′/P′ with S/P and stretching to the right of the figure.

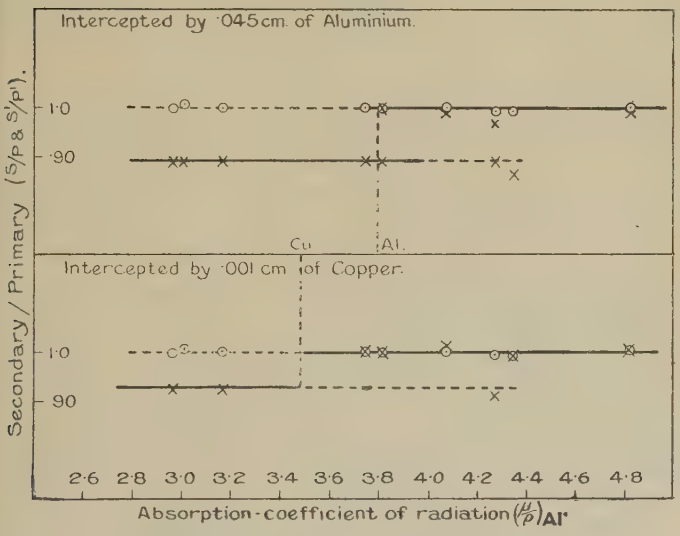
Thus, using any one definite thickness of absorbing substance, the secondary radiation appears softer, *i.e.* more absorbable than the primary, by a series of jumps which occur at the absorption-coefficients, now well known as giving the J discontinuities. This apparent change in the character of the radiation produced by scattering is, however, not what it superficially appears to be, for (1) if it were a true change in the absorbability of the secondary radiation, when it originates it should be observed without the presence of the absorbing sheets. A change in absorbability of a radiation is normally accompanied by a change in the ionization-coefficient for that radiation in a gas, so that a sudden change in the secondary radiation would result in a change in the ratio of ionizations produced by the unintercepted secondary and primary beams unless, as has been indicated, there happened to be also a sudden diminution of intensity exactly compensating for an increase in the absorbability and ionization-coefficient in air; the ratio of ionizations produced by the unintercepted beams shows no such change.

(2) The exact penetrating power of the primary radiation at which the secondary radiation suddenly appears softer, depends to a certain extent on the substance used to test the relative absorptions, *i.e.* on the intercepting substance. Thus, when both beams are intercepted by paper instead of by aluminium, the sudden change appears earlier, *i.e.* for a more absorbable radiation, and when intercepted by copper, it occurs at a more penetrating radiation. This is shown in fig. 4, which exhibits corresponding results obtained by testing the absorption in aluminium and in copper. This, again, is perfectly consistent with the results of other experiments on the J phenomenon. The J phenomenon here occurs in the secondary radiation during transmission through the absorbing paper, aluminium, or copper, and thus appears when the $J_1$ critical point is reached in each of these absorbing substances. It does not occur in the scattering substance.

(3) The critical point at which the secondary suddenly differs from the primary, or shows a sudden increased difference from the primary, depends upon the thickness of the absorbing sheets used to test the absorbability. When thick absorbing sheets are used, the change appears earlier than with thin absorbing sheets, which, again, is perfectly consistent with the laws observed for the J phenomenon. It simply means that when a thick absorbing sheet is used, the heterogeneous X-radiation becomes filtered until the

average absorption-coefficient reaches or passes the critical value for the J phenomenon, while the thin absorbing sheets do not sufficiently change the average absorption-coefficient to take the beam beyond the critical point. In order to do this the radiation must be a little harder than is the case with the thicker absorbing sheet.

Fig. 4.

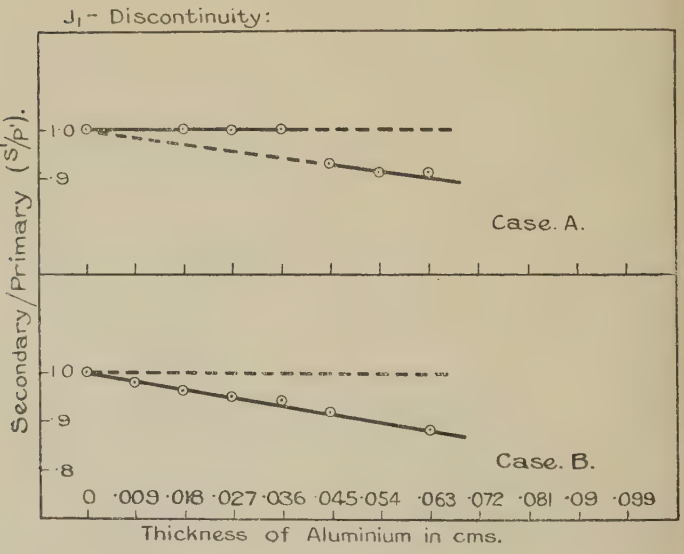



Circles denote "unintercepted ratio" S/P.
Crosses denote "intercepted ratio" S′/P′.

(4) This is most clearly shown by the more direct experiment of keeping the primary radiation unchanged, and gradually increasing the thickness of the absorbing sheets placed in the paths of both primary and secondary radiations, but keeping this thickness the same in the two beams. For when the radiation is somewhat more absorbable than the critical value for the J discontinuity, the thin absorbers indicate no difference between the two, that is S′/P′ is precisely equal to S/P. But as the thickness of the absorber is increased, the critical absorbability is reached by the process of elimination of the softer constituents, and the difference between the secondary and primary radiations suddenly appears in the form of the J discontinuity in the scattered radiation, but not in the primary radiation. Thus,

plotting S′/P′ for different thicknesses of absorbing aluminium, as in fig. 5, Case *a*, the value remains constant until the $J_1$ step is reached, showing that up to this point the secondary and primary radiations are equally absorbable. The value of S′/P′ then drops suddenly, and subsequently diminishes with increase in the thickness of absorbing aluminium, showing the secondary to be then more absorbable than the primary. Thus for such selected radiations thin absorbers showed no difference between scattered and primary

Fig. 5.

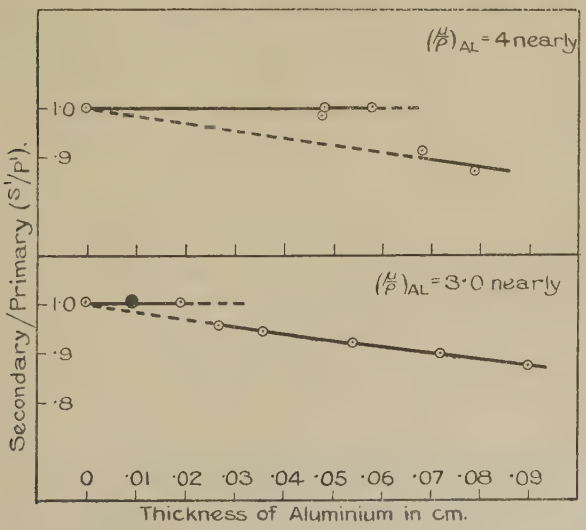



radiations; thick absorbers showed the difference, the latter being separated from the former by the occurrence of the J phenomenon in the absorbing substance.

(5) The magnitude of the sudden fall in the value of S′/P′ depends upon the thickness of absorbing substance already traversed before the discontinuity occurs. Thus, when only a thin sheet was necessary to bring the secondary radiation to its critical absorbability, the drop in the value of S′/P′ was small. When the radiation was absorbable and a thicker sheet was necessary to produce the J discontinuity, the value of S′/P′ fell by a greater amount. In fact, the discontinuity so measured depended in magnitude upon the thickness of absorbing material previously traversed. This was shown both by experiments described above in section (3)—for the

level of the line depends on the thickness of the intercepting sheet—and by the simple filtering experiments. The latter is clearly shown in fig. 6, which brings out the feature that when the discontinuity occurs its magnitude is such as to compensate for what might, under different conditions, have taken place in the absorbing substance already traversed. Thus the sloping portion to the right of the discontinuity is the latter portion of a sloping line starting from the origin. In Case *b*, considered below, in which the J phenomenon did

Fig. 6.




not occur, a difference between the values of S′/P′ and S/P occurred even with the thin sheets (fig. 5, Case *b*). Here the secondary was definitely more absorbable than the primary from the very beginning, but in Case *a*, which we are considering, such a difference between the secondary and primary radiations existed only after the J discontinuity. Such a result suggests that either the last layer of the absorbing sheets necessary to produce the discontinuity precipitates a change which has already been made possible by transmission through the first layers and remains latent until some essential condition is produced, or that the processes taking place in the last layer influence the behaviour of the radiation in the preceding layers ; that is, operate backward and cause the earlier layers to absorb more strongly than they do in the absence of that last critical layer.

As a preliminary investigation of this point, *i.e.* as to

whether the last effective layer influences the action of preceding layers, we separated the absorbing sheets to considerable distances apart, but we found the result unaffected. Though this experiment is not conclusive, we are inclined to regard the last layer as precipitating a transfer of energy of the radiation to certain electrons in the matter traversed; that is, as producing the necessary condition for certain electrons to act as nuclei for condensation of energy from the radiation, a condensation which might under other conditions have occurred in the earlier layers. This condition is provided when the absorption-coefficient of the heterogeneous radiations reaches a certain critical value within the substance traversed. We have already compared this to a condensation (or evaporation) of the energy of the radiation, the energy becoming concentrated in certain electrons *

(6) Again, the discontinuity of figs. 2 and 3 occurs much less frequently when thin absorbing sheets are used than is the case when thick sheets are used. This, indeed, is shown by the results obtained for the "unintercepted" beams, for even these must pass through thin aluminium windows to the measuring electroscopes. In some experiments, these thin electroscope windows did show the $J_2$ discontinuity. That the discontinuity was really due to this thin aluminium window is evidenced by the fact that it was never obtained when the aluminium window was replaced by thin celluloid.

Thus in all these experiments—Case *a*—the apparent difference between the secondary (scattered) X-radiation and the primary X-radiation producing it is a consequence of the transmission of the radiation through the intercepting substance used to test the absorbability of these radiations. All the difference between the two appears abruptly at penetrating powers characteristic of these absorbing substances. Apart from these differences definitely associated with the testing material, the scattered and the primary radiations are exactly alike to a high degree of accuracy. If there be a difference it is less than one-tenth of the difference demanded by Compton's hypothesis, or alternatively there is less than one-tenth of Compton's hypothetical radiation.

### Case *b*.

In many experiments the apparent difference between the secondary and primary radiations appears even for soft—low-frequency—radiation, and persists throughout a very great

* Barkla and Gladys Mackenzie, 'Nature,' June 20, 1925.

range of frequencies. This is the result which makes the nearest approximation to anything of the nature of a change such as is given by Compton's hypothesis. Let us examine it: the facts are these :—

The ratio of ionizations produced by the intercepted secondary and primary radiations ($S'/P'$) is definitely less, and unless the intercepting sheets are very thin, this ratio $S'/P'$ is *markedly* less than $S/P$. The difference between $S/P$ and $S'/P'$ depends, as one would expect, upon the thickness of the intercepting sheets. It indicates a true difference between the absorbabilities of the scattered and the primary radiations as usually measured. Suppose the radiation to be perfectly homogeneous, then the ratio of ionizations of unintercepted beams ($S/P$) is a measure of the relative intensities of secondary and primary radiations, *i. e.*

$$\frac{S}{P} = k\frac{I_s}{I_p}\frac{i_2}{i_1},$$

where $I_s$ and $I_p$ are the intensities of secondary and primary radiations, $i_2$ and $i_1$ the ionizing coefficients of these radiations, and $k$ is a constant depending on the precise arrangement of apparatus ; whereas the ratio of the intercepted beams

$$S'/P' = \frac{k\,I_s\,i_2\,e^{-\mu_2 x}}{I_p\,i_1\,e^{-\mu_1 x}},$$

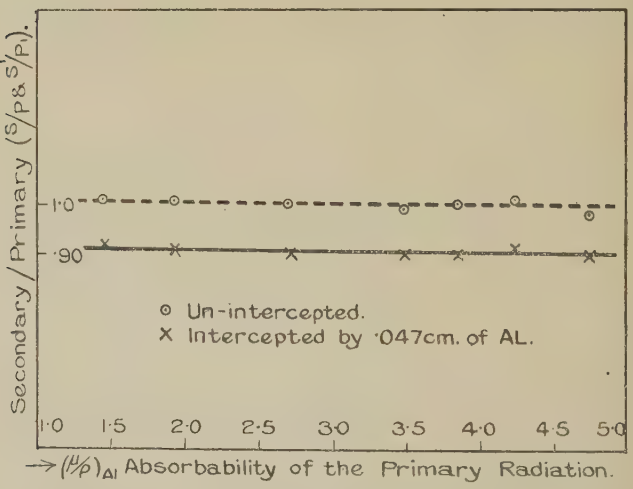
and $$S'/P' \div S/P = e^{-(\mu_2-\mu_1)x}.$$

$1 - \dfrac{S'/P'}{S/P}$ is the fractional fall in the ratio of ionizations due to transmission of both secondary and primary beams through a thickness $x$ of absorbing substance. This would equal $1 - e^{-(\mu_2-\mu_1)x}$, and for small thicknesses should be proportional to the thickness $x$. This is found to be the case ; $\dfrac{S/P - S'/P'}{S/P}$ varies just as we would expect if there were a true transformation of the radiation by scattering.

Such an experimental result as is described as Case *b*, if considered alone, would, of course, lead an observer to the conclusion that there was a change in the absorbability on scattering. But what do we find? The ratio of $S'/P'$ to $S/P$ is precisely the same in Case *b* as when we actually observe the discontinuity in Case *a* : that is, the change from $S/P$ to $S'/P'$ which in Case *b* appears to be produced in the scattering substance, is identical with what in Case *a* we observed to take place in the absorbing substance.

Thus in Case *b*, beginning with low-frequency radiation and gradually increasing the frequency, instead of observing the similarity of secondary and primary radiations at the low-frequency end and the various steps introducing a well-marked difference, we observe even with the softest radiation the difference which, in Case *a*, appears only after the first step, and this difference persists throughout the whole range of frequencies. This is illustrated in fig. 7, in which the ratio for intercepted beams, shown by the crosses, shows no discontinuity at either the $J_1$ or the $J_2$ point through which it passes.

Fig. 7.




It seems highly probable, therefore, that if we could sufficiently extend the range of wave-lengths experimented upon, a step like the $J_1$ step would be observed in the region of very low frequencies.

Be that as it may, the process by which the difference between secondary and primary beams is produced must be identical in the two cases. In cases which we can examine (Case *a*) the change of character is definitely not in the process of scattering. We must therefore conclude that, when the change takes place outside our range of direct experimental investigation, the process is identical in nature, and is therefore still not produced by scattering, or even by any process, call it what we may, by which the scattered radiation originates.

A second point is, that throughout a great range of wave-lengths, indeed throughout the full range of our experiments, the ratio $S'/P' \div S/P$, i. e. $e^{-(\mu_2-\mu_1)x}$, is so accurately constant. In numerous and extensive series of observations this has been most strikingly shown—that whatever the wave-length, the effect on this ratio of intercepting both primary and secondary radiations by a definite thickness of aluminium is independent of the wave-length. In other words, the ionizing power of the secondary radiation after transmission through a definite thickness of aluminium is a definite fraction less than that of the primary radiation similarly treated, whatever the wave-length of the radiation. This does not look like a wave-length change at all, for the result itself is a very simple one, whereas the change of wave-length on scattering required to produce it is not nearly so simple.

Thus let $\lambda_1$ and $\lambda_2$ be the wave-lengths of primary and secondary radiations respectively, and let $\lambda_2=\lambda_1+\delta$.

The coefficients of absorption of these radiations in aluminium may be written, at any rate to a first approximation, as

$$\left(\frac{\mu}{\rho}\right)_1 = k\lambda_1^3 + \frac{\sigma}{\rho} \quad \text{and} \quad \left(\frac{\mu}{\rho}\right)_2 = k(\lambda+\delta)^3 + \frac{\sigma}{\rho},$$

where $k$ is a constant and $\frac{\sigma}{\rho}$ is the scattering coefficient in aluminium. Then

$$\left(\frac{\mu}{\rho}\right)_2 - \left(\frac{\mu}{\rho}\right)_1 = 3k\lambda^2\delta.$$

Experiment shows this to be constant; that is, $\delta \propto \frac{1}{\lambda^2}$.

Thus, to give such a simple experimental result, the change of wave-length on scattering would require to be approximately inversely as the square of the wave-length of the primary radiation. Closer approximation to accuracy would make this only more complicated.

This, again, is entirely at variance with Compton's hypothesis, which leads to the conclusion that $\delta$ is constant, *i. e.* that the change of wave-length on scattering is independent of the wave-length. On Compton's hypothesis $\left(\frac{\mu}{\rho}\right)_2 - \left(\frac{\mu}{\rho}\right)_1$ should then be proportional to $\lambda^2$, and our horizontal lines for $S'/P'$ should be lines sloping down to the right.

Our experimental result, however, is simple, and is simply and accurately described :—The difference between secondary

and primary radiations throughout a long range of wave-lengths is represented by a constant difference of absorption-coefficients. This simplicity of statement implies a simplicity of action. The improbability of a somewhat complicated law expressing the fundamental change of wave-length yielding a result of the simplest possible kind when expressed in terms of absorption-coefficient needs no emphasizing. The constant change of absorbability seems to be the fundamental change.

Again, if the change in the absorbability of the secondary radiation involved a real transformation of this radiation, say a wave-length change, this would necessarily involve also (1) a change in the energy of the radiation, (2) a change in the ionization-coefficient of such a radiation in the gas of the detecting electroscope (for ionization-coefficient normally varies as the cube of the wave-length approximately), as well as (3) a change in the absorption of such radiation in the intercepting sheets.

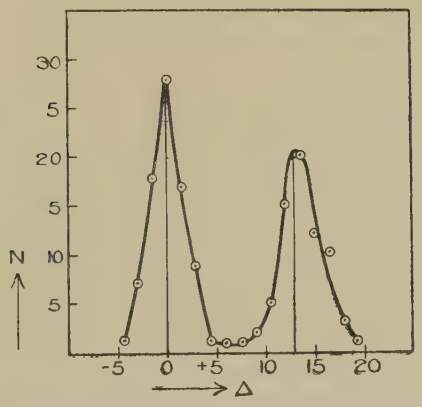
But in Case *a*, in which the change in certain limited regions near the J discontinuity is seen to take place in the absorbing substance, these three would all be effective in producing a difference between S′/P′ and S/P, for when S/P is determined the change has not taken place; whereas in Case *b*, in which any change that there is takes place before the radiation falls on the intercepting sheets, (1) and (2) would have already affected S/P, so that the difference between S/P and S′/P′ would be due to (3) alone. The fact that $\frac{S'/P'-S/P}{S/P}$ is identical in the two cases shows that (1) and (2) are both zero, or just possibly that they neutralize. The latter is most improbable though not impossible. There is a change in absorption-coefficient, but all the evidence is against a change in wave-length.

This is also shown, of course, in the filtering experiment (see figs. 5 and 6) in which the value of S′/P′ is plotted against various values of $x$. When the discontinuity occurs with thin absorbing sheets the J step is certainly small, showing that the combined effect of a possible change of energy and change of ionization-coefficient is exceedingly small. But, though the evidence is strongly against a change of wave-length produced in the $J_1$ transformation, it cannot be regarded yet as completely conclusive. There still appear to be possibilities in connexion with the $J_2$ and $J_3$ transformations to which some of the above considerations do not seem to apply. These need further investigation.

The alternative nature of the two cases (*a* and *b*) is well

illustrated by collecting all the observations, good and indifferent, obtained at various times with various experimental arrangements and showing their distribution. Fig. 8 shows by its ordinates the number of measurements plotted

Fig. 8.




Ordinate: Number of observations within the range of $\pm 0{\cdot}75$ per cent. of abscissa.

Abscissa: Percentage change of absorption-coefficient.

Displacement of $\left(\frac{\mu}{\rho}\right) = 13$ per cent. when $\left(\frac{\mu}{\rho}\right) = 5{\cdot}2$ or $5{\cdot}3$ average, *i. e.* Mo K$\alpha$.

against the observed difference between the absorption-coefficients of secondary and primary radiations when the primary radiation had an absorption-coefficient $\left(\frac{\mu}{\rho}\right)_{Al}$ in the neighbourhood of $5{\cdot}3$, which is the absorbability of Mo "K"-radiation upon which so many spectroscopic measurements have been made. The distribution curve shows two well-marked peaks, one corresponding to an absolutely unchanged radiation, and the other to a definite change of "absorption-coefficient" of 13 per cent.

This is suggestive of Compton's intensity curve showing the peaks obtained in one experiment and appearing to have been obtained simultaneously. In our experiments, however, these are not produced at the same time, but are alternative effects; and, in addition, our modified peak is due to a transformation taking place independently of scattering.

It happens, too, that in this region, where most of Compton's measurements have been made, the magnitude of the separation of our two peaks agrees very well with Compton's theoretical value for the wave-length change. Thus a 13-per-cent. change of absorption-coefficient would correspond to a change of wave-length of a little more than 4 per cent., which is Compton's change for Mo "K"-radiation. It should be noticed, however, that fig. 8 shows the results of our methods at their worst. The best are naturally obtained in one series of observations with one form of apparatus, and when it is found that the X-ray tube is working regularly. Then the two alternative spectral lines are much more clearly marked, and are completely separated by a gap several times the width of either line. The horizontal lines of fig. 3 are in reality such spectral lines—the "unmodified" and the "modified,"—though the method of drawing shows them horizontal instead of vertical. One or two observations, as might be expected, were found between the two peaks, but it was seen in some such cases that a change actually occurred during the experiment, and the final readings were therefore intermediate between the true instantaneous values of the ratio. Such values are, of course, included in fig. 8. It is practically certain that all such intermediate values, as they were so few, were the result of a change of the critical condition during the experiment, the unmodified radiation being effective during one portion of the time, and the modified during the remainder.

## *Summary.*

The simplest and most direct experiments on the scattering of X-rays from paper show that when the scattered radiation is tested there is either (*a*) a very exact equality of penetrating powers of secondary and primary, or (*b*) a well-marked difference between the two. The difference when it appears is the result of the J transformation which occurs in matter during transmission of the radiation through that matter. In many cases, this is definitely subsequent to the emission of secondary radiation from the radiating substance; and in the other cases, although the radiation when first tested appears to have been transformed, the transformation is exactly like that actually seen to occur outside the scattering substance. The transformation then observed is thus not the result of scattering or of any process (call it what we may) by which the radiation originates.

The law giving the difference between the secondary and primary radiations is, as far as it is expressible in familiar terms, that between two J discontinuities the difference between the absorption-coefficients of primary and secondary radiations is a constant, viz.:

$$\left(\frac{\mu}{\rho_2}\right)=\left(\frac{\mu}{\rho_1}\right)+\text{constant.}$$

Thus, though we have made hundreds of comparisons between the secondary and primary X-radiations, we find only the difference due to what we have called the J phenomenon occurring in the scattered radiation. A change of wave-length which, according to Compton, is produced in the process of emission of the secondary radiation, quite clearly and definitely did not occur in such experiments.

It seems highly probable, however, that the displaced spectral line as observed by Compton and others is a result of the J phenomenon, for in place of Compton's results we find something corresponding to them expressible in terms of this much more general J phenomenon.

(1) Thus, instead of Compton's change of wave-length on scattering, we find that a scattered radiation which is indistinguishable from the primary radiation, under some conditions has its absorbability suddenly and definitely changed by transmission through matter. This is the J transformation observed elsewhere.

(2) Instead of the change of wave-length being general, we find the J transformation is conditional on factors other than the nature of substance traversed and wave-length of radiation.

(3) Instead of an unmodified and a modified scattered radiation appearing simultaneously, we find over a short period *either* one *or* the other.

(4) Instead of the primary and scattered radiations being distinguished by a constant difference of wave-length, we find that over the range between two J discontinuities there is a constant difference of absorbability, *i.e.* instead of $\lambda_2=\lambda_1+\text{constant}$, we find

$$\left(\frac{\mu}{\rho}\right)_2=\left(\frac{\mu}{\rho}\right)_1+\text{constant.}$$

(5) To these we may add a preliminary announcement of

the results of experiments conducted with Miss Gladys Mackenzie on the scattering at various angles :—

> Instead of a difference in the wave-lengths of scattered radiations proceeding in directions making angles of 60° and 120° with the primary beam, we find *either* (*a*) the two scattered beams have precisely the same absorbability between J discontinuities, but the beam at 120° shows the discontinuites, the other does not ; *or* (*b*) the radiation at 120° is continuously more absorbable than the other.
>
> This dependence on some unknown critical condition is characteristic of the J phenomenon.

What then is the J phenomenon? It is too new and too comprehensive to describe in a few words. But it appears that all the phenomena due to X-rays—the activity of an X-radiation—depends in part (possibly entirely) on a coherence of constituent radiations, and that a slight change of condition alters the activity of the X-radiation from one definite level to another. There are various levels of activity dependent not on individual harmonic constituents of a complex radiation, but on the radiation as a whole. The J discontinuities are the steps from one level to another, and the change of activity is the J transformation.

As the activity resulting in corpuscular emission, ionization, photographic action, etc., does not vary continuously with wave-length, anomalies may as a consequence appear in spectrometer work. Appreciable refraction may also occur in a crystal when the absorption suddenly changes at a J discontinuity.

Be that as it may (and the suggestions are not too promising), the evidence we have obtained seems strongly against a change of wave-length, at any rate as ordinarily understood, even when the $J_1$ transformation occurs. But the phenomenon is so new and opens up such vast possibilities that we must still regard it as an open question, with the balance of evidence strongly against. This, however, is a question concerned with the J phenomenon and not scattering or anything resembling it, though it is probable that the process of scattering in some cases (Case *b*) produces the necessary condition for a change of activity of the radiation from one level to another, and so indirectly involves the J transformation. Such a transformation may, however, be produced by other means and in radiations other than scattered radiations.

[To be continued.]

CXXI. *On the Energy Distribution Law appropriate to the Theory of Chemical Reaction Velocity.* *By* C. N. Hinshelwood *and* C. W. Thornton *.

THE very great influence of temperature on the rate of chemical change necessitates the conclusion that only molecules endowed with exceptionally large amounts of energy react. The nature of this necessary "energy of activation" is not, in the first instance, specified. It might be kinetic energy of translation or rotation, energy of intramolecular vibration, or electronic energy. It has also been suggested that absorption of infra-red radiation plays its part in promoting chemical change. In this note we confine our attention to bimolecular chemical reactions because here at least the radiation hypothesis seems superfluous, for, from the nature of the case, molecular collisions are necessary, and, as Planck showed long ago, the interchange of energy by collisions in a gas is at all ordinary temperatures vastly greater than any interchange by radiation.

It is customary in chemical calculations to put the fraction of the total number of molecules possessing the energy of activation equal to $e^{-\frac{E}{RT}}$, where E is the unspecified critical energy. In a bimolecular reaction the probability that a molecule (say of "class $\alpha$") will possess energy greater than $E_1$ is $e^{-\frac{E_1}{RT}}$, and the chance that a second molecule (of "class $\beta$") will have energy greater than $E_2$ is $e^{-\frac{E_2}{RT}}$. The chance that the two molecules in collision will be of classes $\alpha$ and $\beta$ respectively is therefore $e^{-\frac{(E_1+E_2)}{RT}}$. We are now concerned not with the separate values of $E_1$ and $E_2$, but with their sum. Thus the expression $e^{-\frac{E}{RT}}$ is equally applicable to bimolecular and unimolecular changes. It cannot, however, be rigidly true for all forms of energy; in the case of kinetic energy of translation, for example, it is only an approximation obtained by projecting the velocities on to a plane. For the rotations of a diatomic gas, on the other hand, it would be rigidly true when due attention is paid to quantum restrictions.

Since in a molecular collision redistribution of all the energy takes place, there seems no reason for neglecting the possibility that molecules with exceptionally high energy of

* Communicated by the Authors.

any of the three kinds may react. Thus :

$$\text{number of molecules reacting} = (\text{number entering into collision}) \times \{P_1 f_1(T) + P_2 f_2(T) + P_3 f_3(T)\}, \quad . \quad . \quad (1)$$

where $f_1(T)$ represents the fraction of the total number of collisions in which the joint kinetic energy of the molecules exceeds $E_1$ and $P_1$ is a factor, independent of temperature, representing the probability that the colliding molecules have suitable orientation. $f_2(T)$ and $P_2$ represent the corresponding quantities relating to rotational energy, and $f_3(T)$ and $P_3$ to vibrational energy. Electronic energy is left out of account, as in ordinary thermal reactions (as distinct from photo-chemical reactions) molecules probably do not suffer electronic excitation of the ordinary kind *.

A satisfactory theory of bimolecular reaction can actually be developed on the basis of the simple equation :

$$\text{number of molecules reacting} = Z \,.\, e^{-\frac{E}{RT}},$$

where Z = the number of collisions.

There are two ways of finding E :—

(1) From the absolute number of molecules reacting, using the above equation.

(2) From the temperature coefficient of the reaction velocity, and the equation :

$$\frac{d(\log k)}{dT} = \frac{E}{RT^2}.$$

The values obtained by the two methods agree well, affording satisfactory confirmation of the theory of activation.

We have used the formula $e^{-\frac{E}{RT}}$ for the number of activated molecules. It is first proposed to investigate whether this has any deeper significance than that $e^{-\frac{E}{RT}}$ is a sufficiently good approximation for a possibly more comcated distribution law. We will assume, therefore, that all the energy of activation is initially brought into the complex of colliding molecules in the form of kinetic energy of translation. In this case the exponential $e^{-\frac{E}{RT}}$ should be replaced by

$$1 + \frac{2}{\sqrt{\pi}} x_0 e^{-x_0^2} - \frac{2}{\sqrt{\pi}} \int_0^{x_0} e^{-x^2} \,.\, dx,$$

* Little appears to be known about the quantum states of the electrons actually involved in binding the atoms together.

where $x_0^2 = \frac{E}{RT}$; for the values of $x_0$ with which we have to deal, the integral

$$\frac{2}{\sqrt{\pi}} \int_0^{x_0} e^{-x^2} \, . \, dx$$

can be replaced by the expansion

$$1 - \frac{e^{-x_0^2}}{\sqrt{\pi}} \left( \frac{1}{x_0} - \frac{1}{2x_0^3} + \frac{3}{4x_0^5} \cdots \cdots \right),$$

giving the complete expression

$$\frac{2}{\sqrt{\pi}} \, . \, e^{-x_0^2} \left( x_0 + \frac{1}{2x_0} \cdots \cdots \right)$$

to replace $e^{-\frac{E}{RT}}$*. If this is used instead of $e^{-\frac{E}{RT}}$, the values obtained by methods (1) and (2) will both be affected and to different extents. It remains to be seen whether the numerical agreement obtained when the simple formulæ are used is seriously affected. In method (1), by employing the usual formula, we should have calculated an erroneous value E′ connected with the true value E by the equation :

$$e^{-\frac{E'}{RT}} = \frac{2}{\sqrt{\pi}} \, . \, e^{-\frac{E}{RT}} \left[ \sqrt{\frac{E}{RT}} + \frac{1}{2\sqrt{\frac{E}{RT}}} \cdots \right],$$

while in method (2), using the ordinary formula, we should have calculated an erroneous value E′, given by

$$\frac{E'}{RT^2} = \frac{E}{RT^2} - \frac{2\frac{E}{RT^2}}{2\frac{E}{RT} + 1} + \frac{1}{2T}.$$

Taking as a basis for calculation the data for three bimolecular reactions (Hinshelwood and Hughes, J. Chem. Soc. cxxv. p. 1841, 1924), the following table shows the influence

* Strictly, when the distribution law for translational energy is used we can no longer fuse the expressions for $E_1$ and $E_2$ into a single expression for E. We assume, therefore, for simplicity, that the sum, E, is contributed nearly all by one molecule. Actually $e^{-\frac{E}{RT}}$ becomes multiplied by a factor which is a function of the *separate* values of $E_1$ and $E_2$. The effect on our ultimate conclusions is inappreciable.

of using the correct distribution law for translational energies instead of the simple exponential formula :—

| Reaction. Thermal decomposition of: | Temperature. (Absolute.) | Value of E (to nearest 100 calories). Method (1) (uncorrected). | Method (1) (corrected). | Method (2) (uncorrected.) | Method (2) (corrected). |
|---|---|---|---|---|---|
| $Cl_2O$..... | 384° | 22,000 | 23,400 | 21,000 | 21,400 |
| HI ..... | 760° | 43,900 | 46,700 | 44,000 | 44,700 |
| $N_2O$ ..... | 956° | 55,000 | 58,600 | 58,500 | 59,400 |

On the whole the agreement of the corrected values of E obtained by the two independent methods is as good as that of the uncorrected.

It must therefore be concluded that :—

($\alpha$) It is not possible to determine from the form of the distribution law whether translational or some other form of energy is directly responsible for molecular activation.

($\beta$) That until values of E can be determined with greater experimental precision, it is justifiable to use the simple formula $e^{-\frac{E}{RT}}$.

It now remains to be seen whether it is possible to distinguish between the cases where one only or all three of the forms of molecular thermal energy may represent energy of activation. We have just seen that the approximate distribution law may be used in each case, so that equation (1) becomes :

$$\text{number of molecules reacting} = n = Ze^{-\frac{E}{RT}}(P_1 + P_2 + P_3).$$

The geometrical "orientation" factors $P_1$, $P_2$, and $P_3$ are probably of the order 0·5 in each case, so that we may put them all equal.

If, then, one form of energy only is effective, we should calculate E from the equation :—

$$n = Z \,.\, P \,.\, e^{-\frac{E_1}{RT}},$$

if three kinds are effective from the equation :

$$n = 3Z \,.\, P \,.\, e^{-\frac{E_2}{RT}}.$$

At 400° absolute, E is of the order of 20,000 calories for

reactions proceeding at conveniently measurable rates. The difference between $E_1$ and $E_2$ calculated by these two equations is less than 1000 calories; it would be difficult experimentally to distinguish with real certainty between say 20,000 and 21,000 obtained from temperature-coefficient measurements. For similar reasons it is impossible to find the precise value of P; we can only find that its order of magnitude is not far removed from unity.

We must conclude, therefore, that, as far as experimental determinations along these lines go, all forms of molecular thermal energy might simultaneously be effective in bringing about the activation of molecules in bimolecular reactions. There remains to consider the question of quantum restrictions. These will be quite unimportant in the case of rotational energy and comparatively unimportant in the case of vibrational energy, because the rotational quantum is of the order of a few hundred calories only, and the vibrational quantum for such molecules as iodine is considerably less than the chemical heats of activation, which range from 20,000 calories upwards. Where thermal activation is concerned, therefore, many quanta are involved. Although the final state of the molecule might be one of electronic activation characterized by a large quantum, we are concerned with the processes which bring this energy to the molecule. These we have assumed to be simple thermal ones.

Trinity College,
Oxford.

---

## CXXII. *On the Fulcher Lines in the Hydrogen Spectrum.*

*By* C. R. Bury, *Lecturer in Physical Chemistry at the University College of Wales, Aberystwyth*.*

REGULARITIES in the many-lined spectrum of hydrogen were first detected by Fulcher [1], who called attention to two closely related groups of triplets in the red and green. The classing together of these lines is justified not only by the mathematical regularity in their distribution, but also by their similar physical characteristics; later work has served only to confirm it.

Fulcher, followed by Allen [2] and Curtis [2], takes the view that these triplets are arranged in two bands: six triplets in the red form Fulcher's first band, four in the green his second band. It is obvious, however, that there are other

* Communicated by the Author.

related lines which find no place in this simple scheme. I wish to put forward another view, that each triplet is only the three brightest lines of a band. In place of Fulcher's ten triplets arranged in two bands, I suggest that there are ten bands arranged in two series, the first series in the red containing six bands (R 1, R 2, ... R 6), the second in the green four band (G 1, ... G 4). Each band consists of two branches ($Q_1$ and $Q_2$), so designated on account of their great resemblance to the $Q_1$ and $Q_2$ branches in the band spectrum of helium described by Curtis [4]. The lines of the $Q_1$ branches are more intense and are more numerous than those of the $Q_2$ branches.

So far as I know, these are the only bands yet described that consist of Q branches alone : a careful search has failed to discover any P or R branches, but it is still possible that these exist and have been overlooked. It is impossible to calculate the moment of inertia of the molecule from Q lines only, so these bands throw little light on the structure of the hydrogen molecule.

The bands have the characteristics that might be expected of the spectrum of a molecule having a small moment of inertia, such as the hydrogen molecule. The wave-numbers and physical properties of the lines forming the most intense band (R 1), taken from the tables of Merton and Barratt [5],

Table I.—R 1 band, wave-numbers, and physical characteristics.

| | $Q_1$ branch. | | | | | | $Q_2$ branch. | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *m*. | Wave-numbers. | Intensity. | High Pressure. | Low pressure. | Condensed discharge. | Helium effect. | Wave-numbers. | Intensity. | High pressure. | Low pressure. | Condensed discharge. | Helium effect. |
| 1... | **16611·43** | 10 | ... | ++ | = | 0 | **16596·41** | 7 | ... | ... | — | ++ |
| 2... | **16574·14** | 10 | ... | + | ... | ++ | 16544·32 | 5 | + | ... | ... | ++ |
| 3... | 16507·73 | 5 | ... | + | ... | ++ | 16464·48 | — | ... | ... | ... | ++ |
| 4... | 16416·37 | 2 | ... | ... | ... | ++ | 16363·53 | 0 | | | | |
| 5... | 16303·85 | 2 | ... | ... | + | | | | | | | |
| 6... | 16172·99 | 0 | ... | ... | ... | + | | | | | | |

are shown in Table I. ; the three most intense lines, which form the Fulcher triplet, are printed in heavy type. As might be expected, each branch contains relatively few lines :

those lines that correspond to the lowest values of the rotational quantum number ($m$) are most intense, and the intensity falls off rapidly with increase of $m$. As is often found, lines corresponding to low values of $m$ are favoured by low pressure ; high pressure and a condensed discharge favour those lines with higher values of $m$ relatively to those with low values of $m$. Most of the lines of these bands are enhanced by the presence of helium.

Schwarzschild's theory of band spectra [6] and Kratzer's half-quantum hypothesis [7] lead to the following equations, in which the notation of Curtis [4] has been adopted :—

$$Q_1(m) = V_0 + c_2 m^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$Q_2(m) = V_0 + c_2/4 + c_2 m + c_2 m^2, \quad . \quad . \quad . \quad . \quad (2)$$

where $Q_1(m)$ and $Q_2(m)$ are the wave-numbers of successive lines of the $Q_1$ and $Q_2$ branches respectively, $m$ is any integer, and $V_0$ and $c_2$ are constants, the latter involving the moments of inertia of the molecule before and after the emission of light.

At first sight it would appear possible to replace the two branches and the two equations by a single branch governed by the equation

$$Q(m) = V_0 + c_2 m^2/4, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where substitution of even numbers for $m$ gives lines of the same frequency as equation (1), and odd numbers the same as equation (2). This is really the structure that is adopted by Allen in his "associated (perpendicular) series," which contain many of the lines that I have classified as belonging to $Q_1$ and $Q_2$ branches, but arranged in a single branch of the type demanded by equation (3). Two facts, however, show that the lines under discussion do not form a single branch: firstly, if the lines are arranged in this way their intensities show a distinct alternation, which is very noticeable in Allen's perpendicular series ; secondly, it is well known that these equations are only approximate, particularly for molecules of small moments of inertia, and for small values of $m$—the differences between the frequencies of the observed lines and those calculated from a suitable equation of type (3) are alternatively large and small. Thus, the intensities of the lines and their deviations from the theoretical formula make it certain that they belong to two branches, not to a single branch.

Search for the missing P and R branches has shown how easy it is, from the 1200 lines in Merton and Barratt's tables, to find a group of five or six lines arranged in accordance with the band law, and how cautious one must be before admitting that any group of lines arranged in this manner has any significance, and is not merely due to chance. The only real proof that these R bands have any significance lies in the fact that there are six parallel R bands: the significance of any one band, if isolated, would be doubtful, but six parallel bands can hardly be a chance arrangement. In Table II. are given the wave-numbers of all the lines in

TABLE II.—Wave-numbers, intensities, and first differences of lines of $Q_1$ branches, R bands.

| Band. | $m=1$ | $=2$ | $=3$ | $=4$ |
|---|---|---|---|---|
| R 1... | **16611·43** (10) | *37·29* **16574·14** (10) | *66·41* 16507·73 (5) | *91·36* 16416·37 (2) |
| | *280·77* | *279·61* | *277·34* | *275·65* |
| R 2... | **16330·66** (10) | *36·13* **16294·53** (8) | *64·14* 16230·39 (4) | *89·67* 16140·72 (0) |
| | *270·35* | *269·18* | *266·71* | *263·52* |
| R 3... | **16060·31** (9) | *34·96* **16025·35** (8) | *61·67* 15963·68 (4) | *86·48* 15877·20 (1) |
| | *259·58* | *258·25* | *256·22* | *250·27* |
| R 4... | **15800·73** (8) | *33·63* **15767·10** (6) | *59·64* 15707·46 (2) | *80·53* 15626·93 (1) |
| | *248·32* | *247·05* | *244·34* | *236·57* |
| R 5... | **15552·41** (5) | *32·36* **15520·05** (3) | *56·93* 15463·12 (0) | *72·76* 15390·36 (0) |
| | *236·48* | *234·98* | | |
| R 6... | **15315·93** (4) | *30·86* **15285·07** (2) | | |

the $Q_1$ branches of the R bands, together with their intensities (in brackets) and their first differences (in italics); the Fulcher lines are printed in heavy type. The regularity in the distribution of these 24 lines, which is more obvious if second differences are taken, proves that the bands have a real existence. The lines of the $Q_2$ branches of the R bands are given in a similar manner in Table III.; they are not so numerous or so powerful as the lines of the $Q_1$ branches. This table includes the line 16315·64, which is anomalous in position and intensity, and has been discussed by Curtis [3]; with this exception the regularity in their wave-numbers is satisfactory.

The G bands, *i. e.*, Fulcher's second band, are not so bright as the R bands, consequently fewer constituent lines have

TABLE III.—Wave-numbers, intensities, and first differences of lines of $Q_2$ branches, R bands.

| Band. | $m=1$ | | $=2$ | | $=3$ | | $=4$ | |
|---|---|---|---|---|---|---|---|---|
| R 1... | **16596·41** (7) | *52·09* | 16544·32 (5) | *79·84* | 16464·48 (–) | *100·95* | 16363·53 (0) | |
| | *280·77* | | *278·52* | | | | | |
| R 2... | **16315·64** (9) | *49·84* | 16265·80 (3) | | | | | |
| | *269·30* | | *268·06* | | | | | |
| R 3... | **16046·34** (7) | *48·60* | 15997·74 (3) | *74·30* | 15923·44 (0) | | | |
| | *259·06* | | *257·23* | | | | | |
| R 4 .. | **15787·28** (5) | *46·77* | 15740·51 (1) | | | | | |
| | *247·85* | | *246·02* | | | | | |
| R 5... | **15539·43** (2) | *44·94* | 15494·49 (0) | | | | | |
| | *235·86* | | | | | | | |
| R 6... | **15303·57** 1) | | | | | | | |

been observed ; they seem, however, to be similarly constituted. All the lines that I have been able to detect have already been described by Allen [2], who classifies them as "associated (perpendicular) series." The alternating intensities of these series shows that the constituent lines belong to branches ($Q_1$ and $Q_2$), not to a single branch, just as with the R bands.

Edward Davies Chemical Laboratories,
University College of Wales,
Aberystwyth.
July 8, 1925.

## REFERENCES.

[1] Astrophys. Journ. xxvii. p. 60 (1913).
[2] Proc. Roy. Soc. A, cvi. p. 69 (1924).
[3] Proc. Roy. Soc. A, cvii. p. 570 (1925).
[4] Proc. Roy. Soc. A, ci. p. 38 (1922) ; ciii. p. 315 (1923).
[5] Phil. Trans. A, ccxxii. p. 369 (1922).
[6] *Vide* Sommerfeld, "Atomic Structure and Spectral Lines," English Edition, 1923, Chapter VII.
[7] *Sitz. d. Bayer. Akad.* March 1922, p. 107.

CXXIII. *Adsorption Forces and their Electrical Nature.—* II. *The Electrical Moment of the Adsorbed Molecule and the Superficial Energy of the Adsorbent. By* Professor Boris Iliin, *The Moscow Institution for Physics and Biophysics*.*

In my preliminary contribution to this Magazine †, based on an electrical theory of adsorption developed by me, definite relations between adsorption-constants—*i.e.* between the adsorption-capacity $C_\infty$ and the heat of adsorption Q and the dielectrical constant of the adsorbed gas $\epsilon$—were given.

For the electrical moment of the adsorbed molecule $\tau = d \cdot \eta'$, where $\eta'$ is the magnitude of the charge at the ends of the dipol, $d$ the distance between charges, a relation was given

$$\tau = \frac{E_0}{4\pi N_L}\left(\frac{\epsilon-1}{\epsilon}\right), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $E_0$ is the tension of the field of adsorption and $N_L$ the Loschmidt-constant.

This theory enables us to determine $E_0$ and therefore to calculate $\tau$. In fact, the heat of adsorption of 1 mol of a gas is

$$Q = S_0\int_0^\infty \frac{E_0^2}{8\pi}\,dx - S_0\int_0^\infty \frac{\epsilon E^2}{8\pi}\,dx$$
$$= \frac{\overline{E_0^2}}{8\pi} S_0\int_0^\infty \frac{\epsilon-1}{\epsilon}\,dx = \frac{\overline{E_0^2}}{8\pi}\frac{\epsilon_0-1}{N_0} S_0\int_0^\infty n\,dx,$$

where $N_0$ is the number of mols of a gas in 1 cm³. at 0° and 76 cm. Hg ; $n$ is the number of mols of a gas in 1 cm³. of the adsorption layer at a given temperature T and a pressure $p$ ; $\epsilon_0$ and $\epsilon$ are items for the dielectric constant for $N_0$ and $n$ correspondingly.

Because $S_0\int_0^\infty n\,dx = 1$ mol of gas, therefore

$$Q = \frac{\overline{E_0^2}}{8\pi}\cdot\frac{\epsilon_0-1}{N_0},$$

and therefore

$$\frac{\overline{E_0^2}}{8\pi} = \frac{QN_0}{\epsilon_0-1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* Communicated by the Author.
† Phil. Mag. xlviii. p. 193, July 1924.

On replacing Q by experimental data obtained by A. Titoff for adsorption of gases by coal, and the values of Q for adsorption of gases by mica, according to Langmuir's data, we get the average value for coal $\frac{\overline{E_0^2}}{8\pi} = 1{\cdot}1 \,.\, 10^{10} \frac{\text{erg}}{\text{cm}^3.}$, and for mica $\frac{\overline{E_0^2}}{8\pi} = 0{\cdot}6 \,.\, 10^{10} \frac{\text{erg}}{\text{cm}^3.}$.

Inserting these values into the formula (1), we get the *absolute* values for the electrical moments of the adsorbed molecule of different gases in the field of adsorption for coal or mica (see Tables I. and II.).

TABLE I.

The electrical moments of the adsorbed gas-molecule for adsorption by coal.

| | $H_2$. | A. | $N_2$. | CO. | $CH_4$. | $CO_2$ | $C_2H_4$. |
|---|---|---|---|---|---|---|---|
| Q in cal..... | 2408 | 3990 | 4270 | 4860 | 5570 | 6560 | 7800 |
| $(\epsilon_0-1).10^6$.. | 264 | 557 | 581 | 695 | 944 | 985 | 1312 |
| $\tau.10^{19}$ ..... | 4·1 | 8·7 | 9·1 | 10·9 | 14·8 | 15·4 | 20·5 |

TABLE II.

The electrical moments of the adsorbed molecule for adsorption by mica.

| | $H_2$. | A. | $N_2$. | CO. | $CH_4$. | $CO_2$. | $C_2H_4$ |
|---|---|---|---|---|---|---|---|
| Q. in cal..... | — | 1530 | 2390 | 2990 | 3090 | — | — |
| $\tau.10^{19}$..... | 3·0 | 6·4 | 6·6 | 7·9 | 10·8 | 11·2 | 15·0 |

From the above tables, we can see that the electrical moment $\tau$ of the adsorb-ion (we designate by the name of adsorb-ion the adsorbed molecule) has a size $10^{-18}$–$10^{-19}$, and consequently the distance between the displaced charges in the molecule $d = \frac{\tau}{\eta}$ is of the order $10^{-9}$ cm., *i.e.* it has a sufficient space for its distribution in the volume of the gas-molecule (the diameter of the molecule is $\sim 10^{-8}$ cm.).

Table III. gives for comparison the different values for $\tau$ and $d$, obtained by different authors out of different phenomena.

Equation (2) gives us the average density of the volume energy at the surface of the adsorbent. If it is multiplied by the thickness of the adsorbing layer $r_0$ we get the density

TABLE III.

| | E. RUTHERFORD and R. K. McKLING, 1900 (from adsorption of X-rays in gases). | M. REIGANUM, 1903 (from internal friction of gases). | P. DEBYE, 1912 (the dependance of dielectric constant upon temperature). | M. JONA, 1919 | B. ILIIN. (from adsorpti |
|---|---|---|---|---|---|
| | —— | —— | 3·4 ($CH_3OH$) | 3 ($CO_2$) | 4-20 (coal) |
| $r \cdot 10^{19}$ | —— | —— | 11·8 ($C_2H_5OC_2H_5$) | 15·3 ($NH_3$) | 3–15 (mica) |
| | | | | 18·7 ($H_2O$) | |
| | | 0·39 ($H_2$) | | 0·6 ($CO_2$) | 0·9 ($H_2$ by coa |
| $d \cdot 10^{19}$ | 1·1 ($CO_2$) | 1·07 ($CO_2$) | 1·1 | 3·3 ($NH_3$) | 3·2 ($CO_2$ by co |
| | | 1·19 ($C_2H_4$) | | 4·0 ($H_2O$) | 4·4 ($C_2H_4$ by c |

of the surface energy, or in its first approximation the value of the surface-tension $\sigma$ of the *solid* adsorbent :

$$\sigma \cong \frac{\overline{E_0^2}}{8\pi} \cdot r_0 = \frac{QN_0}{\epsilon_0 - 1} \cdot r_0. \quad . \quad . \quad . \quad . \quad (3)$$

For low temperatures

$$C_\infty = S r_0 n_0 e^{\frac{Q}{RT}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $C_\infty$ is the adsorption-capacity, S the adsorbing surface of 1 gr. of coal, $n_0$ the concentration of a gas in an exterior space.

Calculating here from $r_0$ and inserting it in equation (3), we get

$$\sigma \cong \frac{C_\infty}{S} \frac{QN_0}{\epsilon_0 - 1} \frac{1}{n_0} e^{-\frac{Q}{RT}}. \quad . \quad . \quad . \quad . \quad (5)$$

S, according to our calculations *, is of the order $10^5$ cm$^2$. Inserting numerical data, we get an average for coal : $\sigma \cong 1000 \frac{\text{erg}}{\text{cm}^2}$.

The Moscow Institution for Physics and Biophysics,
Moscow, 3 Miusskaja 3 (Russia)
(formerly the Physical Institution of the
Science Institution of Moscow).

* B. Iliin, *Zeit. phys. Chem.* xvi. p. 431 (1925).

CXXIV. *Contribution to the Kinetic Theory of Vaporization.* —II. *By* Samuel Clement Bradford, *D.Sc., The Science Museum, London, S. W. 7* *.

IN a previous paper † the kinetic theory was applied to obtain an expression for the vapour-pressure of a liquid in terms of molecular attraction, volume, and motion. However, the formula deduced was applicable only to liquids having densities between 0·6 and 1·0. It has now been extended to include liquids of any density.

The liquid, in contact with its vapour only, is supposed to be maintained at a constant temperature within a thermostat under ordinary laboratory conditions, so that if heat be abstracted from the liquid by the escaping particles of vapour, it will be supplied immediately by the enclosure, while any heat gained by the vapour will be given up to the surroundings.

In consequence of the electrical structure of matter, molecules within a liquid will be attracted on all sides by molecules near enough for their attraction to be appreciable, and the average value of the resultant of this attraction will be zero. When, however, a molecule approaches the free surface of the liquid to a distance less than the limit of molecular attraction, the downward attraction will not be balanced by an equal attraction above, consequently the molecule will experience a resultant attraction towards the liquid and normal to its surface. Such a molecule will not be able to escape into the vapour unless its velocity is sufficient to enable it to overcome the force normal to the surface.

If all the molecules of the liquid are in continuous rapid motion, their rotational velocity will maintain a clear spherical space around the centre of rotation of each molecule. As the molecules are electrically neutral, they will repel in some orientations and attract in others. Because the duration of the attractive encounters is greater, the attractions will preponderate over the repulsions. Let $\delta$ be the mean of the nearest distances of approach of the centres of two molecules during a considerable number of encounters. If we consider a space element $dv$ at a definite position relative to a given molecule, the molecules with their centres within $dv$ will be continually changing their position and attractive forces. During a sufficiently long

* Communicated by the Author.

† Phil. Mag. xlviii. p. 936 (1924).

interval of time, any point within $dv$ will have been occupied by a molecular centre as often as any other point, and the average force at that point will be the same as at any other point. In measuring the vapour-pressure of liquids we are concerned, not with instantaneous values, but with average values during a considerable interval of time. It seems legitimate, therefore, to consider the average values of the molecular forces within a given space element. The space element $dv$ may be situated at any distance from an attracted molecule equal to, or greater than, $\delta$.

The average attraction* between two molecules whose centres are at a distance $r$ has been shown to be

$$f = \frac{c}{r^8}, \quad \ldots\ldots\ldots \quad \text{(i)}$$

where

$$c = \frac{6K\delta^4}{\varpi N^2} \quad \ldots\ldots\ldots \quad \text{(ii)}$$

K being the cohesion of the liquid and N the number of molecules per unit volume.

To find the attraction of the liquid on an escaping molecule, let P be the centre of a molecule at a distance $x$ below the surface AB of the liquid, where $x > \delta$. The attraction of the liquid on P may be taken as equal and opposite to the attraction that would be exerted by a continuous mass of liquid above AB. Molecules in this supposed liquid, whose centres would be between two planes parallel to AB, at distances $\xi$ and $\xi + d\xi$ above AB, would exert on P a resultant attraction equal to

$$\frac{2\varpi c N d\xi}{(x+\xi)^6} \int_0^\pi \cos^6 \sin\theta \, d\theta = \frac{2\varpi c N \, d\xi}{7(x+\xi)^6}.$$

The attraction per unit area on P by all the molecules whose centres would be above AB would be equal to

$$\frac{2\varpi c N}{7} \int_0^\infty \frac{d\xi}{(x+\xi)^6} = \frac{2\varpi c N}{35 x^5}. \quad \ldots\ldots \quad \text{(iii)}$$

When the distance below the surface AB of the escaping molecule becomes less than $\delta$, that part above AB of a sphere, with radius $\delta$ described around the molecule, will contain no centres of attracting molecules. The attracting molecules above AB may now be considered to have their centres within the portions above AB of two spheres, with

* Edser, "Molecular Attraction and the Physical Properties of Liquids." Brit. Assoc. 4th Report on Colloid Chemistry, p. 40 (1922).

radii $r$ and $r+dr$ described around the molecule at P. The resultant attraction on P by molecules whose centres would be between these spheres is

$$\frac{2\varpi c\mathrm{N}dr}{r^6}\int_0^{\cos^{-1}\left(\frac{x}{r}\right)}\cos\theta\sin\theta\,d\theta=\frac{\varpi c\mathrm{N}\,dr}{r^6}\left(1-\frac{x^2}{r^2}\right),$$

and the total attraction on the molecule by all molecules whose centres would be above AB is

$$\varpi c\mathrm{N}\int_\delta^\infty\left(\frac{1}{r^6}-\frac{x^2}{r^8}\right)dr=\varpi c\mathrm{N}\left\{\frac{1}{5\delta^5}-\frac{x^2}{7\delta^2}\right\}. \quad . \quad . \quad . \quad \text{(iv)}$$

The work done by the molecule at P in escaping to the surface of the liquid is, therefore,

$$\frac{2\varpi c\mathrm{N}}{35}\int_{-\infty}^{-\delta}\frac{dx}{x^5}+\varpi c\mathrm{N}\int_{-\infty}^{0}\left(\frac{1}{5\delta^5}-\frac{x^2}{7\delta^2}\right)dx=\frac{\varpi c\mathrm{N}}{6\delta^4}. \quad . \quad \text{(v)}$$

An equal amount of work must be done by the molecule in escaping completely from the surface to infinity, so that, neglecting the small attraction of the vapour, the total work done by a particle of liquid in passing into the vapour is

$$\mathrm{W}=\frac{\varpi c\mathrm{N}}{3\delta^4}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vi)}$$

Giving N its value $6{\cdot}23\times10^{23}\,\frac{\rho}{\mathrm{M}}$, $\rho$ being the density of the liquid, and M its molecular weight, we have, from (ii),

$$\mathrm{W}=3{\cdot}21\times10^{-24}\,\frac{\mathrm{MK}}{\rho}. \quad . \quad . \quad . \quad . \quad . \quad \text{(vii)}$$

The number of particles able to escape from the surface can be found from Maxwell's law of the distribution of velocities. The number of particles in unit volume of the liquid that have velocities whose vertical components lie between $u$ and $u+du$ is

$$\frac{n_s}{\mathrm{V}_{ps}}e^{-\frac{u^2}{\mathrm{V}_{ps}^2}}du, \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(viii)}$$

where $n_s$ is the concentration of the liquid particles, and $\mathrm{V}_{ps}$ Maxwell's most probable speed of the particles. Therefore the number of particles per unit volume, having velocities normal to the surface between $u$ and $u+du$, that strike the surface from below is

$$\frac{n_s}{\mathrm{V}_{ps}\sqrt{\varpi}}e^{-\frac{u^2}{\mathrm{V}_{ps}^2}}u\,du. \quad . \quad . \quad . \quad . \quad . \quad \text{(ix)}$$

But of these, only those having velocities normal to the surface, equal to, or greater than, a certain critical velocity, $s$, will be able to escape from the attraction of the liquid and pass into the vapour. The total number of such particles is

$$\int_s^\infty \frac{n_s}{V_{ps}\sqrt{\varpi}} e^{-\frac{u^2}{V_{ps}^2}} u\,du = \frac{n_s V_{ps}}{2\sqrt{\varpi}} e^{-\frac{s^2}{V_{ps}^2}}. \quad . \quad . \quad . \quad . \quad (x)$$

Now the total number of particles from the vapour that strike the same area of the surface is

$$\int_0^\infty \frac{n_s}{V_{pl}\sqrt{\varpi}} e^{-\frac{u^2}{V_{pl}^2}} u\,du = \frac{n_l V_{pl}}{2\sqrt{\varpi}}, \quad . \quad . \quad . \quad . \quad (xi)$$

where $n_l$ is the concentration of the vapour and $V_{pl}$ Maxwell's constant for the vapour phase.

The greater attraction of the liquid ensures that all particles striking the surface from above return to the liquid. In equilibrium the number of particles escaping from the liquid must be equal to the number returning, so that from (x) and (xi)

$$\frac{n_s V_{ps}}{2\sqrt{\varpi}} e^{-\frac{s^2}{V_{ps}^2}} = \frac{n_l V_{pl}}{2\sqrt{\varpi}}$$

or

$$n_l = n_s \frac{V_{ps}}{V_{pl}} e^{-\frac{s^2}{V_{ps}^2}}. \quad . \quad . \quad . \quad . \quad . \quad (xii)$$

Now Kleeman * has shown that the most probable speed of the particles is not the same in all substances or in different states of matter, because the particles do not remain at equal distances apart, nor, indeed, do the attractive forces remain constant. Therefore, except when passing through points at which the instantaneous forces vanish, the particles are under the influence of attraction and their most probable speed is affected by the attraction. Therefore, in equation (xii), we may not write $V_{ps} = V_{pl}$, but

$$V_{ps} = \lambda V_{pl}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (xiii)$$

where $\lambda$ is a factor that will vary with the nature of a substance and its state.

If $v_l$ be the volume occupied by the number, N, of molecules in a gramme molecule of the given substance

* Phil. Mag. xxiv. p. 101 (1912).

in the vapour state, and $v_s$ the volume of the same number of molecules in the liquid condition, then

$$n_l = \frac{N}{v_l - b_l} \quad \text{and} \quad n_s = \frac{N}{v_s - b_s},$$

where $b$ and $b_s$ are the apparent volumes of the molecules in either state, defined by Kleeman* as the quantities whose magnitudes affect the external pressure at constant temperature and volume, but not the average velocity of translation of the molecules. Putting

$$v_s - b_s = \Phi_s \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xiv)}$$

and

$$v_l - b_l = \Phi_l, \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xv)}$$

equation (xii) becomes

$$\Phi_l = \frac{\Phi_s}{\lambda} e^{\frac{s^2}{\lambda^2 V_{pl}^2}}. \quad . \quad . \quad . \quad . \quad . \quad \text{(xvi)}$$

As a first approximation, we may take $V_{pl}$, the most probable speed of the particles in the vapour, as equal to $V_p$, the most probable speed in a perfect gas, so that

$$V_{pl}^2 = \left(\frac{V}{1{\cdot}23}\right)^2,$$

where V is the average kinetic energy velocity in the gaseous state and is determined by the equation

$$\tfrac{1}{2} m V^2 = 2{\cdot}012 \times 10^{-16} T,$$

$m$ being the absolute weight of a particle and T the absolute temperature.

Now the critical velocity $s$ fulfils the relation

$$\tfrac{1}{2} m s^2 = W,$$

as given by equation (vi). Making use of these relations, equation (xvi) becomes

$$\Phi_l = \frac{\Phi_s}{\lambda} e^{\frac{7{\cdot}52 \times 10^{19} W}{\lambda^2 T}} \quad . \quad . \quad . \quad . \quad . \quad \text{(xvii)}$$

But the pressure of the vapour in atmospheres is

$$p = 81{\cdot}84 \frac{V_t}{V} \frac{T}{\Phi_l},$$

where $V_t$ is Kleeman's total average velocity of a molecule in the vapour, and is taken as approximately equal to V.

* 'A Kinetic Theory of Gases and Liquids,' New York, 1920.

From equations (vii) and (xvii) we have, therefore,

$$p = 81{\cdot}84\,\frac{T\lambda}{\Phi_s}\,e^{-\frac{2{\cdot}414\times10^{-8}KM}{\lambda^2\rho T}} \quad . \quad . \quad . \quad \text{(xviii)}$$

It has been shown that the cohesion K can be calculated with considerable accuracy from Edser's equation,

$$K = \frac{4S}{\delta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xix)}$$

where S is the surface tension and $\delta$ is given by the formula

$$\delta = \left(\frac{3{\cdot}24M}{2{\cdot}016\rho_m}\right)^{1/3}\times10^{-8}, \quad . \quad . \quad . \quad . \quad \text{(xx)}$$

$\rho_m$ being the density of the liquid near the freezing point. Writing

$$\delta' = \delta\times10^8 \quad \text{and} \quad \frac{M}{\rho} = v_s,$$

the pressure of the vapour becomes

$$p = 81{\cdot}84\,\frac{T\lambda}{\Phi_s}\,e^{-\frac{9{\cdot}656Sv_s}{\lambda^2T\delta'}}.$$

This applies to a non-associated liquid. Should the liquid be associated, its molecular weight would be A . M, where A is the degree of association and M the molecular weight of the unassociated substance. So that the molecular and co-volumes of an associated liquid become $Av_s$ and $A\Phi_s$ respectively. Similarly, the average molecular diameter becomes $A^{1/3}\delta$. It should be noticed that A is not an arbitrary factor, but represents the actual physical state of the liquid. Therefore the vapour pressure in atmospheres of an associated liquid is

$$p = 81{\cdot}84\,\frac{T\lambda}{\Phi_sA}\,e^{-\frac{9{\cdot}656Sv_sA^{2/3}}{\lambda^2T\delta'}} \quad . \quad . \quad . \quad . \quad \text{(xxi)}$$

This formula assumes that for every particle, associated or unassociated, that approaches the surface of a liquid with a velocity normal to the surface equal to, or greater than, the critical velocity $s$, a single particle is communicated to the vapour. The assumption is not entirely without justification. But the complete analysis would require a knowledge of the actual values of the attractions of the associated and unassociated particles, and at present these data are lacking. However, when A is small the expression

is approximately correct, as the table below will show ; and the values of A required to satisfy the formula are found to be almost exactly those determined by Ramsay and Shields*. The values of $\Phi$ are given approximately by the relation †

$$\Phi = v - \frac{\delta^3}{4}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xxii)}$$

In the equation (xxi) there is unfortuuately one variable, $\lambda$, that is practically unknown. This function, the ratio of the total average velocity of the molecules in the given liquid to that in a perfect gas, was calculated from theoretical considerations by Kleeman to be 1·6 for $CO_2$ at 112 atmospheres and 40°. By another method he obtained a higher figure. However, even the lower figure is rather too high for the vapour-pressure formula. It is necessary, moreover, to find an expression for the variation of $\lambda$ with the nature and condition of the liquid. The relation assumed in the previous paper agreed extraordinarily with the experimental data for densities between about 0·66 and 0·90, but began to break down as the density increased beyond the latter figure.

It seemed desirable, therefore, to study the values of $\lambda$ required by the formula for as many as possible different liquids within wide limits of density and temperature. If the vapour-pressure of a liquid is dependent merely on molecular attraction, volume, and motion, $\lambda$ can be a function of these variables only. However, after an exhaustive study of a considerable number of substances, no simple relation could be found at the higher densities, and a flaw in the formula was suspected. This was very kindly indicated by Dr. J. H. Shaxby, who pointed out corrections to equations (vii) and (xiii) of the previous paper which have been incorporated in equations (xvi) and (v) of the present article.

These alterations introduce the necessary very slight modification in the vapour-pressure formula which takes the form of equation (xxi) above. Within the range of densities previously considered, the new formula requires little alteration in $\lambda$. For instance, the new values of $\lambda$ for benzene, toluene, and pyridine become 1·36, 1·39, and 1·34 respectively, instead of 1·39, 1·34, and 1·36. For higher densities a definite relation between $\lambda$ and $\rho$ can now be traced. As a temperature coefficient is indicated, the values of $\lambda$ were calculated for a number of practically

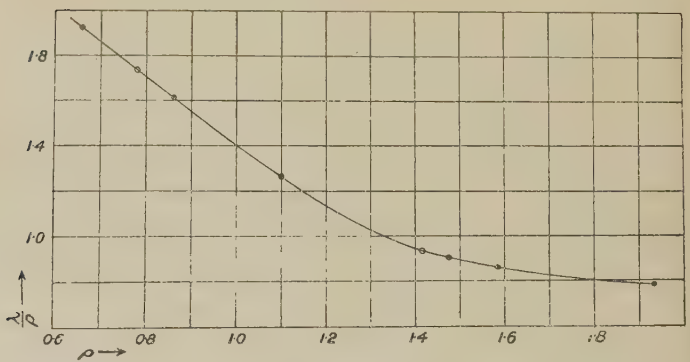
* J. C. S. lxiii. p. 1089 (1893).
† Bradford, Phil. Mag. xlviii. p. 944 (1924).

unassociated liquids at about 25°, using Ramsay and Shields' figures for the association, as given in Table I. Plotting $\frac{\lambda}{\rho}$ against $\rho$, the smooth curve shown in fig. 1 was obtained.

TABLE I.

| Substance. | $t$. | $\rho$. | $\lambda/\rho$. |
|---|---|---|---|
| *n*-Hexane | 20° | 0·660 | 1·922 |
| Toluene | 109 | 0·780 | 1·736 |
| | 26 | 0·860 | 1·610 |
| Chlorobenzene | 25 | 1·101 | 1·260 |
| Chloroform | 61·2 | 1·414 | 0·930 |
| | 25 | 1·476 | 0·900 |
| Carbon tetrachloride, (A = 1·01) | 25 | 1·585 | 0·858 |
| Ethyl iodide | 20 | 1·934 | 0·784 |

Fig. 1.




The black circles correspond to values of $\lambda$ at 25° or 20°; the open circles to values at other temperatures reduced to 25° by means of the empirical equation

$$\lambda_t = \lambda_{25} - (0{\cdot}0_3 44 + 0{\cdot}0_3 1\rho)(t-25), \quad . \quad . \quad \text{(xxiii)}$$

$t$ being the centigrade temperature. The points corresponding to the open circles were added as a check. This curve shows that, approximately at least, $\lambda$ is a function of density and temperature only. It follows that

the vapour pressure of a liquid is determined completely by molecular attraction, volume, and motion.

It is to be hoped that further research may throw more light on the ratio of the total average velocities. In the meantime, the curve shown above allows the approximate determination of $\lambda$ for use with the vapour-pressure formula. For convenience in calculation, the values of $\lambda$ at different densities have been tabulated from the curve in Table II.,

Table II.

| $\rho$. | $\lambda/\rho$. | $\lambda$. |
|---|---|---|
| 0·66 | 1·920 | 1·267 |
| 0·80 | 1·702 | 1·362 |
| 0·90 | 1·546 | 1·391 |
| 1·00 | 1·396 | 1·396 |
| 1·10 | 1·251 | 1·376 |
| 1·20 | 1·130 | 1·356 |
| 1·30 | 1·026 | 1·334 |
| 1·35 | 0·980 | 1·323 |
| 1·40 | 0·942 | 1·319 |
| 1·45 | 0·910 | 1·320 |
| 1·50 | 0·886 | 1·329 |
| 1·60 | 0·854 | 1·360 |
| 1·90 | 0·784 | 1·490 |

instead of introducing an algebraical expression for $\lambda$ into formula (xxi). Intermediate values may be obtained by interpolation. Using values of $\lambda$ obtained from the curve in fig. 1, and corrected for temperature by formula (xxiii), the vapour-pressures in Table III. were calculated from equation (xxi). As in the previous paper, the data for the surface tensions and densities were taken from Jaeger's * results ; the other figures from Landolt and Börnstein's 'Tabellen.' Except for hexane, the highest figure in the third column of the table is the boiling-point of the liquid.

It will be seen that the agreement between the calculated and observed values of the vapour-pressures is remarkable, and that the magnitude of the association required by the formula is almost exactly that obtained by Ramsay and Shields.

* *Zeitschr. anorg. Chemie*, ci. p. 1 (1917).

TABLE

| Substance. | Molecular weight M. | Temperature Centigrade $t$. | Density $\rho$. | Molecular volume $v$. | $\delta'$. |
|---|---|---|---|---|---|
| Acetone | 58·05 | 56° | 0·710 | 81·76 | 4·618 |
| | | 20 | 0·778 | 73·30 | |
| Aniline | 93·04 | 184 | 0·867 | 107·31 | 5·283 |
| | | 148·8 | 0·902 | 103·15 | |
| | | 100 | 0·949 | 98·04 | |
| | | 54·8 | 0·990 | 93·98 | |
| | | 43·1 | 1·000 | 93·04 | |
| Benzene | 78·05 | 80·5 | 0·810 | 96·36 | 4·946 |
| | | 74·6 | 0·817 | 95·53 | |
| | | 55 | 0·841 | 92·80 | |
| | | 35·1 | 0·862 | 90·54 | |
| | | 25·1 | 0·873 | 89·40 | |
| Carbon disulphide | 76·12 | 46·8 | 1·224 | 62·19 | 4·618 |
| Carbon tetrachloride | 153·8 | 76·4 | 1·489 | 103·29 | 5·313 |
| | | 25 | 1·585 | 97·03 | |
| Chlorobenzene | 112·5 | 131 | 0·985 | 126·90 | 5·417 |
| | | 25 | 1·101 | 102·18 | |
| Chloroform | 119·51 | 61·2 | 1·414 | 84·46 | 4·994 |
| | | 35 | 1·459 | 81·91 | |
| | | 25 | 1·476 | 80·97 | |
| Ethyl acetate | 88·06 | 77·1 | 0·816 | 107·90 | 5·360 |
| | | 25·1 | 0·893 | 98·61 | |
| Ethyl alcohol | 46·05 | 78·4 | 0·737 | 62·48 | 4·641 |
| | | 25 | 0·786 | 58·59 | |
| Ethyl ether | 74·08 | 34·8 | 0·698 | 106·13 | 5·277 |
| | | 29·5 | 0·703 | 105·38 | |
| | | 25·3 | 0·707 | 104·78 | |
| | | 0·2 | 0·735 | 100·80 | |
| | | −20·5 | 0·758 | 97·30 | |
| | | −75 | 0·818 | 90·56 | |
| Ethyl iodide | 152·88 | 72·5 | 1·830 | 83·55 | 5·000 |
| | | 20·4 | 1·934 | 79·04 | |
| Nitrobenzene | 123·06 | 209 | 1·031 | 122·62 | 5·473 |
| | | 100 | 1·125 | 109·87 | |
| *n*-Hexane | 86·12 | 20 | 0·6595 | 130·58 | 5·905 |
| Phosphorus trichloride | 137·42 | 77·4 | 1·471 | 93·04 | 5·026 |
| Pyridine | 75·05 | 114·5 | 0·882 | 89·73 | 4·911 |
| Toluene | 92·06 | 109·4 | 0·780 | 118·13 | 5·383 |
| | | 26 | 0·860 | 107·05 | |
| Water | 18·02 | 100 | 0·958 | 18·80 | 3·079 |
| | | 20 | 0·998 | 18·06 | |
| *p*-Xylene | 106·08 | 136·2 | 0·757 | 140·13 | 5·555 |

III.

| Co-volume Φ. | Surface tension S. | λ. | Association A. | | Vapour-pressure p. | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Calculated. | | Observed. | |
| | | | From vapour-pressure. | R. & S. | Atmospheres. | mm. | Atmospheres. | mm. |
| 57·14 | 19·4 | 1·29 | 0·96 | | 1·00 | | 1·00 | |
| 48·68 | 23·1 | 1·365 | 1·28 | 1·26 | | 191 | | 180 |
| 71·07 | 24·3 | 1·30 | 1·00 | 1·05 | 1·00 | | 1·00 | |
| 66·91 | 26·8 | 1·33 | 1·13 | | | 289 | | 277 |
| 61·80 | 34·2 | 1·36 | 1·08 | | | 40 | | 46 |
| 57·74 | 39·5 | 1·39 | 1·11 | | | 4 | | 4 |
| 56·80 | 40·8 | 1·39 | 1·19 | | | 1 | | 1 |
| 66·09 | 20·7 | 1·34 | 1·02 | 1·01 | 1·00 | | 1·00 | |
| 65·26 | 21·6 | 1·34 | 1·02 | | | 657 | | 631 |
| 62·53 | 23·8 | 1·37 | 1·02 | | | 387 | | 327 |
| 60·27 | 26·3 | 1·38 | 1·02 | | | 152 | | 148 |
| 59·13 | 27·7 | 1·39 | 1·02 | | | 84 | | 95 |
| 35·77 | 27·3 | 1·38 | 1·24 | 1·07 | 1·00 | | 1·00 | |
| 65·80 | 20·2 | 1·31 | 1·01 | 1·01 at 46° | 1·01 | | 1·00 | |
| 59·54 | 25·4 | 1·36 | 1·01 | | | 118 | | 116 |
| 87·16 | 19·0 | 1·33 | 1·05 | 1·03 | 1·00 | | 1·00 | |
| 62·44 | 32·9 | 1·39 | 1·00 | | | 12 | | 12 |
| 53·32 | 21·8 | 1·29 | 1·00 | — | 1·03 | | 1·00 | |
| 50·77 | 24·8 | 1·32 | 1·00 | | | 341 | | 308 |
| 49·83 | | 1·33 | 1·00 | | | 207 | | 204 |
| 69·4 | 17·2 | 1·36 | 1·27 | 0·99 | 1·00 | | 1·00 | |
| 60·1 | 22·2 | 1·39 | 1·30 | | | 96 | | 95 |
| 37·49 | 17·0 | 1·31 | 2·14 | 2·43 | 1·01 | | 1·00 | |
| 33·60 | 21·3 | 1·35 | 3·20 | 2·74 at 46° | | 60 | | 59 |
| 69·39 | 15·9 | 1·29 | 1·03 | 0·99 | 1·00 | | 1·00 | |
| 68·64 | 16·4 | 1·30 | 1·03 | | | 632 | | 625 |
| 68·04 | 16·7 | 1·31 | 1·04 | | | 531 | | 540 |
| 64·06 | 19·2 | 1·34 | 1·05 | | | 185 | | 186 |
| 60·99 | 21·5 | 1·36 | 1·06 | | | 66 | | 67 |
| 53·82 | 28·5 | 1·42 | 1·09 | | | 0·9 | | 0·9 |
| 52·30 | 22·3 | 1·41 | 1·33 | 0·96 | 1·00 | | 1·00 | |
| 47·79 | 28·1 | 1·52 | 1·00 | 1·00 at 46° | | 104 | | 108 |
| 81·63 | 21·2 | 1·30 | 1·18 | 1·13 at 153° | 1·00 | | 1·00 | |
| 68·88 | 29·0 | 1·35 | 1·01 | 0·93 at 78·4° | | 20 | | 21 |
| 79·1 | 17·41 | 1·27 | 1·00 | | | 114 | | 120 |
| 61·30 | 21·9 | 1·30 | 1·00 | 1·02 at 46° | 0·95 | | 1·00 | |
| 63·12 | 25·2 | 1·34 | 1·02 | 0·93 at 46° | 1·03 | | 1·00 | |
| 79·14 | 19·5 | 1·30 | 1·00 | — | 1·00 | | 1·00 | |
| 68·06 | 28·4 | 1·385 | 1·00 | | | 28 | | 29 |
| 11·50 | 58·92 | 1·36 | 1·82 | 2·66 | 1·00 | | 1·00 | |
| 10·76 | 70·60 | 1·40 | 2·02 | 3·68 | | 17·6 | | 17·5 |
| 97·28 | 18·1 | 1·285 | 0·92 | — | 1·00 | | 1·00 | |

*Summary.*

The vapour-pressure of liquids is a function of molecular attraction, volume, and motion only. The vapour-pressure in atmospheres is expressed by the formula

$$p = 81{\cdot}84\frac{T\lambda}{A\Phi}e^{-\frac{9{\cdot}656SvA^{2/3}}{T\delta'\lambda^2}},$$

where

T is the absolute temperature,
$\lambda$ the ratio of the total average velocity of the molecules in the liquid under the given circumstances to that in a perfect gas,
A is the actual state of aggregation of the molecules in the given liquid,
$\Phi$ the co-volume of the liquid,
S its surface tension,
$v$ the volume of a gramme molecule, and
$\delta' \times 10^{-8}$ the nearest distance of approach of the centres of the molecules in the liquid.

It has been shown that $\lambda$ is a function of density and temperature only, and the relation between these three variables has been traced.

The vapour-pressures of a number of liquids at widely differing temperatures have been calculated by means of the formula and agree remarkably with the observed values.

---

## CXXV. *A Note on the Vibration of the $CO_3$ Group.*

*By* P. A. Taylor, *B.A., Emmanuel College, Cambridge* *.

THE difficulty of explaining the observed infra-red vibrations of the $CO_3$ group in crystals on a simple theory has been clearly brought out in the preceding paper by Chapman and Ludlam †. The present investigation, begun independently, leads to similar conclusions; the numerical results may be of interest as further illustration of the difficulty.

The most obvious deficiency in Kornfeld's treatment of this problem is the neglect of the repulsive fields between the oxygen ions. The writer has introduced the necessary modifications into Kornfeld's analysis to supply this deficiency

* Communicated by Prof. S. Chapman, F.R.S.

† Chapman and Ludlam, Phil. Mag. October 1925, p. 822.

in the same way as that in which Chapman and Ludlam have done in the preceding paper. The force between oxygen ions was taken as $\lambda_n r^{-n}$, while that between oxygen and carbon ions was taken to be $\lambda_m r^{-m}$. A recent investigation † provides numerical values of $\lambda_n$ and $n$, and similar methods lead also to values of $\lambda_m$ and $m$, viz.

$$\lambda_n = 1{\cdot}77 \,.\, 10^{-87},\ n = 11\ ;\quad \lambda_m = 1{\cdot}26 \,.\, 10^{-97},\ m = 12.$$

We introduce these into the generalized equations and so make a fresh determination of $r$ and $\omega_1$, using the numerical value of $\alpha$, the coefficient of polarization, given by Kornfeld ‡. Instead of Kornfeld's agreement between theory and observation being improved, as was expected, the discrepancy is made worse. The figures obtained are given in the following table :—

| | Calc. (this paper) | Calc. (Kornfeld) | Obs. |
|---|---|---|---|
| $r$ ..... | $1{\cdot}07 \,.\, 10^{-8}$ | $1{\cdot}52 \,.\, 10^{-8}$ | $1{\cdot}25 \,.\, 10^{-8}$ (*) |
| $\omega_1$ ..... | $9{\cdot}47 \,.\, 10^{14}$ | $1{\cdot}81 \,.\, 10^{14}$ | $1{\cdot}63 \,.\, 10^{14}$ |

* W. L. Bragg, Proc. Roy. Soc. A, cvi. p. 356. Other observed values are noted in Kornfeld's paper.

In view of the large discrepancy in $\omega_1$ another method was tried. In the preceding work the values assumed for $\lambda_m$ and $\alpha$ were not known with certainty. We substitute for the other constants and obtain equations of the form

$$r = f(\lambda_m,\ \alpha)$$
$$\omega_s = f_s(\lambda_m,\ \alpha) \ldots\ldots s = 1,\ 2,\ 3.$$

Eliminating $\lambda_m$ we may take $r$ and $\alpha$ as unknown parameters and write

$$\omega_s = \phi_s(r,\ \alpha) \ldots\ldots s = 1,\ 2,\ 3.$$

Substituting the observed values of $\omega_1$, $\omega_2$, $\omega_3$, we obtain the three equations

$$\alpha_s = g_s(r) \ldots\ldots\ldots s = 1,\ 2,\ 3.$$

These three relations should be approximately consistent, if our assumptions are correct. If the three equations are exhibited as curves in the $r\alpha$-plane, we should expect them

† Jones and Taylor, Proc. Roy. Soc.
‡ Kornfeld, *Zeit. f. Phys.* xxvi. p. 210 (1924).

to meet, either in a point or in a small triangle. Actually we find that for the only reasonable range of $r$ the curves are more or less parallel. This will be seen from the following table. Lower values of $r$ than those shown make $g_1(r)$ always negative, whereas $\alpha$ is an essentially positive constant.

| $r \cdot 10^8$..... | 1·50 | 1·60 | 1·70 | 1·80 | 1·90 |
|---|---|---|---|---|---|
| $g_1(r) \cdot 10^{24}$ ..... | −1·84 | −0·54 | 1·11 | 3·34 | 6·38 |
| $g_2(r) \cdot 10^{24}$ ..... | 25·1 | 42·7 | 65·7 | 96·3 | 136·5 |
| $g_3(r) \cdot 10^{24}$ ..... | −1·77 | 0·51 | 4·76 | 10·2 | 17·3 |

## CXXVI. *The Influence of the Surrounding Medium on Frictional Electricity.* *By* J. Herbert Jones, *M.A.* (*Cantab.*), *M.Sc.* (*Wales*)*.

THE experiments described in the present paper were made with the object of discovering whether the quantity of electricity developed by friction between two given surfaces depends upon the nature of the medium in which the surfaces are immersed. Although a number of important quantitative results in connexion with frictional electricity have been arrived at in recent years, it cannot be said that there is at present a satisfactory theory as to the manner in which electricity is produced by friction. Mr. M. Owen investigated the relation between the amount of mechanical work done in friction and the quantity of frictional electricity produced on one of the rubbing-surfaces. Owen's experiments were apparently the first in which absolute measurements of frictional electricity were ever made. Mr. Morris Jones, using a method of measurement similar to that of Owen, made comparative measurements of the frictional electricity developed on the surface of various elements by a given quantity of work done in friction by a given rubber. One result arrived at by Morris Jones was that platinum rubbed by silk showed more charge than any other substance rubbed by the same material. So far as the writer is aware, the question of a possible influence of the surrounding medium on the amount of frictional electricity

* Communicated by the Author. Thesis approved for the M.Sc. degree in the University of Wales.

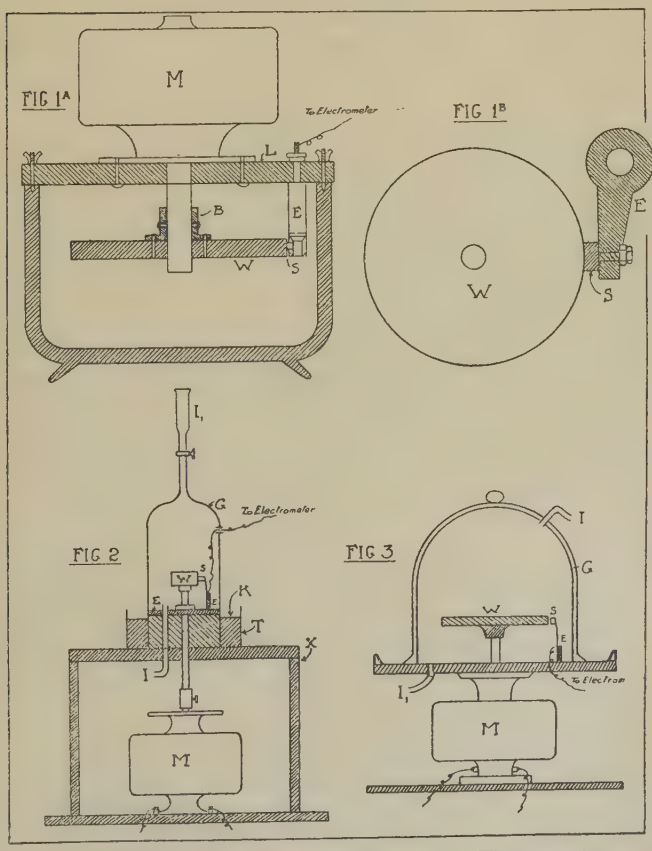
produced has only been examined by McClelland and Power, but those experimenters do not appear to have arrived at any very definite conclusion on the subject.

The whole subject of frictional electricity is at present in a purely experimental stage, and it is hoped that the experiments here described may throw some light on the matter.

## *Apparatus.*

The apparatus used in the present experiments was designed so that the specimen and rubber were enclosed throughout

Figs. 1*a*, 1*b*, 2 & 3.




the measurements in an air-tight vessel. The specimen and rubber could thus not only be surrounded by various gaseous or liquid media, but also thoroughly shielded from variation of climatic conditions.

The first form of apparatus (figs. 1*a* and 1*b*) consisted

essentially of an ordinary motor jet interrupter, with the rotating nozzles and blades removed, and replaced respectively by a rubbing-wheel and the specimen. The ebonite cover L closed air-tight on the iron vessel and carried the motor M, the armature axle of which passed through a stuffing-box (not shown) in L and carried at its lower end the rubbing-wheel W. The specimen S—usually a disk of platinum or copper—was mounted at the end of an ebonite lever E (fig. 1*b*), which was supported by an ebonite pillar E (fig. 1*a*), which passed through a bush in the plate L, allowing the specimen to be pressed on the wheel or separated from it at will. A thin wire passing through E and $E_1$ connected the specimen to a terminal T on the cover. Connexion with the electrometer was made by a wire leading from T, this wire being thoroughly insulated and shielded from external electrostatic influence by earthed metal tubes in the usual way.

The diameter of the wheel used in the first apparatus was about 4 inches. Later it became desirable to use wheels of smaller diameter, and the apparatus was modified accordingly.

Fig. 2 shows the second form of apparatus. In this case the rubbing-wheel was attached to the upper end of the armature-spindle which passed tightly through a rubber stopper R, fitting into the lower end of a wide glass tube G. The lower end of G was embedded in paraffin-wax contained in a metal vessel T, which rested on the platform X. Attached to the upper end of the rubber stopper was an ebonite plate E, which served to support the specimen S which was held in contact with the wheel by a spring, as shown in fig. 2. Connexion with the electrometer was made by a wire attached to the spring and passing through a wax plug filling a hole in the side of the glass tube.

For rubbing-wheels of greater diameter than 4 inches a third form of apparatus was designed. It was essentially the same as that of fig. 2 but was made larger, a bell-jar taking the place of the glass tube of fig. 2. Details of the third apparatus are shown in fig. 3.

In all three forms of apparatus the vessel enclosing the wheel and specimen was practically air-tight, and was furnished with inlet and outlet tubes for the introduction of different gases. The first form of apparatus was suitable for liquid media.

### *The Rubbing-Wheels.*

In the course of the experiments wheels of various kinds and diameters were employed, their materials being ebonite, slate, copper, and wood, their diameters 8 inches,

4 inches, and 1 inch. Most of the wheels were about 1·8 cm. thick, the diameter of the specimen (*i.e.* the platinum disk) being about 1 cm. In the earlier experiments the wheels were used without any covering, but this plan was soon abandoned, and in all the later experiments the rim of each wheel was covered first with a strip of cotton or woollen cloth, over this being wrapped a strip of silk. The kind of silk used was what the makers call, I believe, a "9-m/m gauge"; it was found to be most suitable because more durable than any other kind. Considerable care had to be exercised in the wrapping of the silk, to avoid any seams which might lead to the silk being torn under the vigorous rubbing to which it was subjected.

### *The Electrometer.*

A Dolezalek electrometer of the usual construction was found to be much too sensitive for the present work. Not only were the deflexions much too great, but owing to excessive swinging of the "needle" this sometimes came into contact with one of the quadrants, with a deleterious effect on the battery—a dry-cell battery of 108 volts. Again, the potential developed was sometimes sufficient to cause short sparks to pass between adjacent quadrants. Accordingly, the instrument was considerably modified, and in its final form was arranged as follows :—

The usual fine suspending-wire was replaced by a bifilar suspension consisting of two parallel strips of phosphor bronze. Instead of the usual light paper needle it appeared desirable to use one which was heavier and which was made of some high resistance material. Many kinds of needles were tried, the one finally selected being of slate. This material showed quite sufficient conductivity for the purpose, and gave uniformly consistent and reliable results. For damping, a vane attached to the needle and dipping into some castor-oil contained in an insulated vessel below the needle was found to be quite suitable. All four quadrants were displaced outwards from their centre so that the gap between adjacent quadrants was 7 mm. With these modifications the instrument proved to be suitable both in sensitiveness and reliability for all the purposes of the experiments.

### *Preliminary Experiments.*

The first experiments were made with an ebonite wheel, rubbed directly by the platinum specimen. With this

arrangement no satisfactory result could be obtained, the electrometer sometimes showing a deflexion, sometimes not, and generally behaving in an erratic manner*.

It was found that some improvement could be effected by the use of an earth-connected tinsel brush touching the wheel at the point diametrically opposite to the specimen. It appears that the brush removed a part of the charge developed on the wheel, but it was obvious that it did not remove this charge completely, the electrometer readings being still rather unsteady.

Another method tried was to cover the specimen with flannel and in place of the brush to use an insulated plate supported near, but not in contact with, the wheel. This plate instead of the specimen was now connected to the electrometer. The insulated plate, being under the influence of the charge on the wheel, might be expected to give a measure of the quantity of electricity developed. With this method fairly large deflexions were observed for a time, but after a few thousand turns of the wheel the deflexions fell to zero, the friction afterwards failing to generate any charge. This effect is probably connected with a kind of "electric fatigue" of the ebonite, already noticed by Owen and Morris Jones. If the wheel were allowed to remain at rest for a while, or if its surface was renewed by filing or by warming, it was found to become active once more. An attempt to avoid this effect by covering the ebonite wheel with silk, and again using the uncovered platinum specimen, did not lead to much better success. It was then decided to abandon the ebonite wheel and to try a wheel of wood. The use of a wooden wheel covered with silk and a specimen of platinum or copper caused an immediate and marked improvement; the electrometer deflexions were both larger and steadier. The reason appears to be that some degree of conductivity in the wheel is necessary in order to allow the charge produced upon it by friction to escape through the axle.

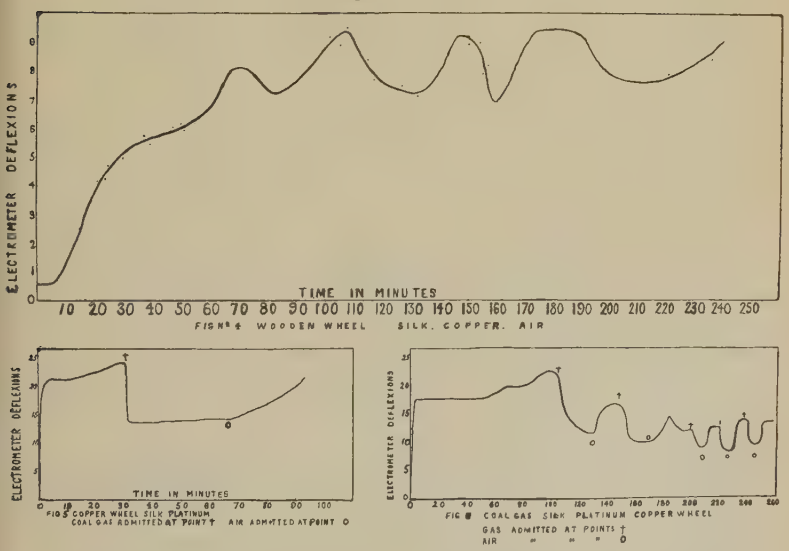
Wheels of copper and of slate were also tried with good results, and in the experiments to be described wheels of one or the other of these three materials (wood, copper, or slate) covered with silk were used throughout. The ebonite wheel was also used in the experiments in oil, the specimen being the disk of platinum or copper.

* Similar results were observed by Messrs. McClelland and Power, Royal Irish Academy, April 1918, when a semi-insulator (wood) was used.

*Method of taking observations.*

It was thought that the best method of comparing the effects of the introduction of different media would be to observe the potential of the specimen, as indicated by the electrometer deflexions, at regular intervals while the wheel was rotating, and to observe the effect of a change of the medium without stopping the wheel. Consequently in each of the curves showing the results of the present experiments the abscissa represents time in minutes, measured from the moment when the rotation began, and the ordinate represents the electrometer deflexions, which were read every minute or half minute. The electrometer was read with a telescope and scale in the usual way.

Figs. 4, 5 & 6.


ELECTROMETER DEFLEXIONS
TIME IN MINUTES
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250
FIGS 4 WOODEN WHEEL SILK. COPPER. AIR
ELECTROMETER DEFLEXIONS
TIME IN MINUTES
FIG 5 COPPER WHEEL SILK PLATINUM
COAL GAS ADMITTED AT POINT †
AIR ADMITTED AT POINT O
ELECTROMETER DEFLEXIONS
FIG 6 COAL GAS SILK PLATINUM COPPER WHEEL
GAS ADMITTED AT POINTS †
AIR " " " O

The sensitiveness of the electrometer was normally such that five divisions on the scale represented 15·7 volts. The insulation of the specimen (separated from the wheel) and its connecting-wire were tested at frequent intervals. Fig. 4 shows a typical curve obtained when the wheel and specimen were surrounded by air. In this diagram most of the observed points lay on the curve, and the others are also indicated. The curve in fig. 4 shows a rather gradual rise of potential to a maximum followed by fluctuations of considerable magnitude, the interval between successive maxima

being about thirty minutes. The cause of these fluctuations was not definitely ascertained ; they might have been due to the rubbing away of entire layers and the formation of new surfaces in the silk material, or possibly, to the "electric fatigue" already mentioned.

The initial rise of potential varied greatly in different experiments—it was always greater with new silk than with old.

*Coal-Gas.*

The method of procedure in this experiment was to set the wheel revolving in air until the potential produced had reached a constant value, which usually happened in about thirty minutes, and then to admit the coal-gas. In this experiment the copper wheel and platinum disk were used. The result is shown in fig. 5, which shows the rapid initial rise of potential followed by the more gradual approach to the steady value. The coal-gas was admitted at point †, when the potential immediately dropped to a certain value, at which it remained constant so long as the gas was allowed to remain in the vessel. At the point ○ the gas was cut off, and by opening a tap fitted in the cover air was allowed to leak in gradually. As the air drives out the gas the curve rises steadily to the previous maximum.

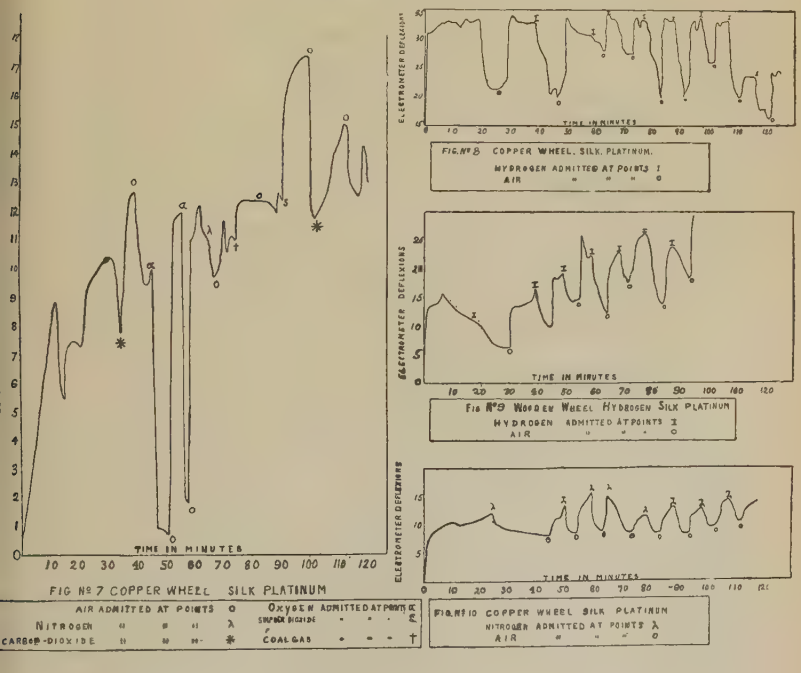
The gradual rise of potential after the point ○ shows the effect of the increasing supply of air. In another experiment with the same materials the results were as shown in fig. 6. In this instance the potential did not rise immediately to the same value as in the previous experiment, but instead, the curves, after rising almost perpendicularly within the first two minutes as before, flattened out at 17·5 divisions, and remained at that value to the 40th minute. Coal-gas was admitted at this point. This was followed, not by a sudden drop as on the previous occasion, but by a gradual rise in potential, and after the gas was cut off at point ○ the rise was maintained up to the 100th minute. Gas was then readmitted, and now the curve bends downward, though not perpendicularly, till the 130th minute, when the gas was cut off again. Instead of allowing the air to leak in gradually it was forced in by means of a bellows, thus clearing out the gas more expeditiously. The curve rose sharply, not gradually as in fig. 5. Gas (†) and air (○) were admitted alternately during the rest of the experiment, the bellows being used at ○ on each occasion. This gave a curve of deep depressions. It will be noticed that the crests do not reach the height attained at the 100th

minute, probably owing to the effect of the gas upon the material, but that the successive heights are approximately equal, just as the minimums of the curves are approximately the same. There is another peculiarity in the results obtained in the experiment, viz., the upward rise on the first introduction of gas at the 40th minute. This phenomenon will be discussed later. It seems to occur with very fair regularity when any gas is introduced except oxygen and ozone.

*Hydrogen.*

Fig. 8 shows the curve obtained with the same wheel and specimen as in the last experiment, when hydrogen was

Figs. 7, 8, 9 & 10.




substituted for the coal-gas. The curve shows a rapid rise as on the previous occasion during the first minute, when the wheel runs in air. The curve gradually reaches a steady value at the end of about twenty minutes. At point I hydrogen was admitted, and immediately the curve takes a downward turn. The gas was allowed to flow slowly through the vessel for seven minutes, and at the end of that period it was cut off

and blown out of the apparatus with the bellows. The curve now turns sharply upward, reaching its highest value at the end of four minutes, and remains nearly horizontal for the next nine minutes, when on the gas being re-admitted the curve drops to approximately the same minimum as before, rising again to its former value on admission of air.

An examination of the rest of the curve will show a similar drop every time the gas is admitted, a similar rise on the admission of air. The heights of the crests in all cases are approximately the same, and the troughs are also approximately at the same level. Any variations are probably due to the amount of gas contained in the vessel.

*Hydrogen.—Wooden Wheel.* (Fig. 9.)

When a wooden wheel was substituted as base for the silk, the gas had a similar effect to that described for the copper wheel, except that there was a tendency for the curve as a whole to go up slowly to the end of the 100th minute. This is clearly shown in fig. 9. It will be noticed that the potential produced by this wheel in the early part of the experiment was not nearly so high as that produced by the copper one. This may have had something to do with the upward tendency of the curve. The troughs in the curve due to the introduction of the hydrogen also are by no means so regular in this experiment.

*Nitrogen.—Copper Wheel.* (Fig. 10.)

Fig. 10 shows the curve obtained with a copper wheel as basis for the silk and the platinum specimen, but with nitrogen as the gas. As before, the wheel was kept running until the specimen reached a fairly steady potential, when the gas was admitted at the point λ. The curve then takes a downward direction at first sharply, then more gradually while the gas remains in the vessel, *i.e.* for about twenty minutes. When the gas is stopped at the point B and is cleared out of the vessel the curve takes a sharp upward turn during the next minute, then remains steady for three minutes, rising again during the next minute. At this point, viz., the 50th minute, gas was again admitted, and it again produced the downward turn. Thus with alternate gas and air a fairly regular curve was obtained. The time during which the gas was allowed to remain in the vessel varied, as in every other experiment, so as to make sure that the drop was due to the gas.

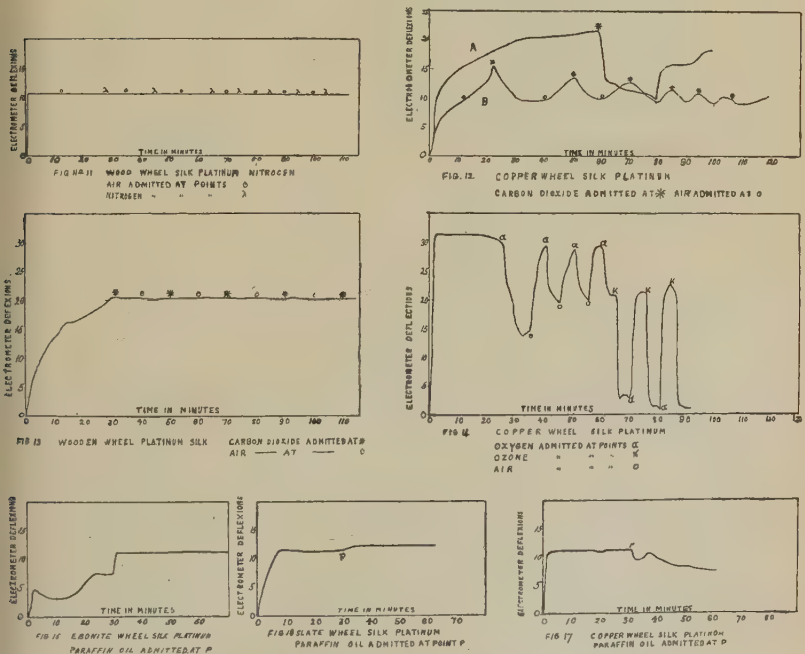
*Wooden Wheel and Nitrogen.*

The curve produced by the wooden wheel as basis for the silk with the platinum specimen was, after the initial rise, practically a horizontal straight line. The admission and removal of the gas were accompanied by very small undulations in the curve, which are indicated by the dots in fig. 11. The gas was admitted at each point marked λ and removed at each point marked ○.

*Carbon Dioxide.* (Fig. 13.)

In this experiment a wooden wheel was used as basis for the silk, platinum being the specimen. After the initial rise

Figs. 11, 12, 13, 14, 15, 16 & 17.


TIME IN MINUTES
WOOD WHEEL SILK PLATINUM NITROGEN
AIR ADMITTED AT POINTS ○
NITROGEN " " " λ
A
B
COPPER WHEEL SILK PLATINUM
CARBON DIOXIDE ADMITTED AT ✳ AIR ADMITTED AT ○
WOODEN WHEEL PLATINUM SILK CARBON DIOXIDE ADMITTED AT ✳
AIR —— AT —— ○
COPPER WHEEL SILK PLATINUM
OXYGEN ADMITTED AT POINTS α
OZONE " " " κ
AIR " " " ○
EBONITE WHEEL SILK PLATINUM
PARAFFIN OIL ADMITTED AT P
SLATE WHEEL SILK PLATINUM
PARAFFIN OIL ADMITTED AT POINT P
COPPER WHEEL SILK PLATINUM
PARAFFIN OIL ADMITTED AT P

in air lasting thirty minutes, carbon dioxide gas was admitted at the point ✳ (fig. 13). Then at intervals of ten minutes the gas was blown out (○) and re-admitted a number of times. In this case, as in that of nitrogen with the wooden wheel, the curve was practically a horizontal straight line, showing only very slight fluctuations of potential due to the change of medium.

When, however, the wooden wheel was replaced by one of copper it was found that carbon dioxide produced a very marked effect on the amount of frictional electricity developed on the platinum specimen. This is shown in fig. 12, curve B, in which the points * are those at which the $CO_2$ was admitted, the points ○ those at which the gas was blown out and replaced by air. The changes of gas took place at irregular intervals, and the regularity with which the fluctuations of potential accompany the changes of medium leaves no room for doubt that the medium has an influence on the amount of frictional electricity produced.

In fig. 12, curve A, the initial rise of potential took place in still air, as usual, but during the interval from the 25th to to the 60th minute *air* was blown through the vessel.

The object of this was to show that a current of air does not cause any depression in the curve. The introduction of the air current does not, in fact, cause any interruption of the gradual initial rise of potential. At the point * in curve A the $CO_2$ was admitted, and the potential immediately fell; at ○ air was re-admitted, and the curve rose again in accordance with the indications of curve B.

### *Oxygen and Ozone.*

The result of one experiment with oxygen and ozone is shown in fig. 14 (copper-silk wheel). The first maximum of potential was unusually high on this occasion, probably because a new piece of silk was used.

Oxygen was admitted at each of the points $\alpha$, and at the point ○ this gas was blown out and replaced by air. The curve shows clearly that the introduction of oxygen causes a marked diminution in the amount of frictional electricity, and that the removal of the oxygen always causes an increase. The same is shown in the curve of fig. 7, in which also the points $\alpha$ indicate the admission of oxygen. In all cases it was found that oxygen produced a diminution of the frictional electricity as compared with air, whether the potential of the specimen were previously high or low. In this respect the effect of oxygen differs from that of some other gases, which may cause a drop of potential if the initial potential is high, and the opposite effect if the originial potential is low.

At the point K in fig. 14 ozone was admitted to the vessel. The ozone was produced by subjecting the oxygen, on its way to the vessel, to the silent discharge from an

induction-coil. It will be seen that the effect of the ozone is to cause the potential to drop immediately almost to zero. The remainder of the curve represents the effect of alternations between oxygen and ozone, the former gas regularly causing a rise to the former value for oxygen, the latter a fall almost to zero.

It appears from this experiment that a medium of ozone is very unfavourable to the production of frictional electricity. It was suspected that the fall of potential at admission of oxygen or ozone might be due to leakage through these gases, and in order to test this, these gases were blown at the "plate" of a charged gold-leaf electroscope. No movement of the leaves resulted, either in this experiment or when the gas was blown, between the electroscope plate and an earthed plate held just above it. It appears, therefore, that the very marked effect of the admission of oxygen or ozone into the friction vessel was not due to leakage from the specimen, or the connecting wires through these gases, but must arise from a difference in the amount of frictional electricity produced in these gases.

### *Sulphur Dioxide.*

This gas would seem to be the best medium for the production of frictional electricity, better even than air.

Introduction of sulphur dioxide when the wheel is running in air and giving either a high or a low potential will immediately cause that potential to be increased.

This effect is shown in fig. 7, in which the point S indicates the moment at which the sulphur dioxide gas was admitted. It seems possible that the improvement which followed the introduction of $SO_2$ might be due to the greater conductivity of this gas, which might remove some of the opposite kind of electricity produced on the wheel. According to this view the $SO_2$ gas acts in much the same manner as the brush held in contact with the wheel, as already described.

A similar effect is also produced when the friction takes place in ordinary paraffin lamp-oil, as described in the next section.

### *Ordinary Paraffin Lamp-Oil.*

The apparatus of fig. 1 was used for liquid media. As usual the wheel was first run in air, and when the potential had become steady the oil was quickly admitted, the speed of the wheel being adjusted to be the same in oil as in air.

Fig. 15 shows the result for the ebonite–silk wheel and

the platinum specimen, the paraffin oil being admitted at the point P. The oil causes an immediate rise of potential, which was afterwards maintained at a very steady value.

It is probable that (as in the case of $SO_2$) the lamp-oil (an imperfect insulator) acts by removing some of the electricity on the wheel. This view seems to be confirmed by the observation that if the vessel is insulated during the friction in oil, the vessel becomes charged, as shown by the electroscope connected with it.

When the experiment was repeated with the slate wheel substituted for the ebonite, the effect of the lamp-oil was much smaller. This result is to be expected since the slate wheel (a much inferior insulator to ebonite) itself allows some of the surface charge to escape to the axle, leaving less to be removed by the oil.

With the copper wheel, however, the results were different (see fig 17). In this case the admission of the oil at P causes a *reduction* of potential of the disk, the potential afterwards slowly declining to the end of the experiment. In this case probably the copper wheel effectively removes all the electricity on the wheel, so that there is none left to be removed by the oil, which then allows some of the charge on the *specimen* to leak away.

The result was again different when the wooden wheel was used (see fig. 18). In this case the introduction of the oil caused no change of potential, the potential remaining constant to the end of the experiment. Here there is apparently a kind of balance between the leakage effects of the wheel charge through the axle, and the specimen charge through the oil.

### *Pure Paraffin Oil.*

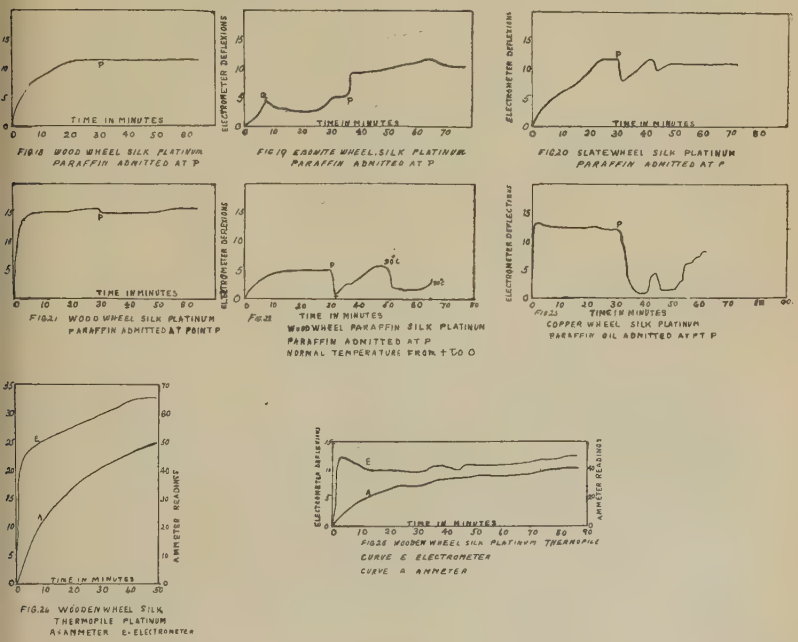
This oil is a much better insulator than the lamp-oil, and consequently it was expected that no marked rise of potential would follow the admission of the oil. The contrary, however, occurred (see fig. 19). The admission of the oil at P causes an immediate rise of potential almost reaching as high a value as in the lamp-oil, though not so steady. In this experiment the ebonite–silk wheel was used.

In this case it is unlikely that any appreciable leakage occurred through the oil, and probably there is a change in the actual amount of frictional electricity produced in this medium.

With the slate wheel the admission of paraffin oil caused a drop of the potential which, however, recovered after a time,

and after some fluctuation finally reached a steady value. These effects are shown in fig. 20. A similar effect is found with the wooden wheel (fig. 21), the fluctuations being, however, less marked. It does not seem possible to account for the effects of pure paraffin oil on the leakage theory, which seemed to fit in with the observations when lamp-oil was the medium.

Figs. 18, 19, 20, 21, 22, 23, 24 & 25.


TIME IN MINUTES
ELECTROMETER DEFLEXIONS
P
FIG 18 WOOD WHEEL SILK PLATINUM PARAFFIN ADMITTED AT P
FIG 19 EBONITE WHEEL SILK PLATINUM PARAFFIN ADMITTED AT P
FIG 20 SLATE WHEEL SILK PLATINUM PARAFFIN ADMITTED AT P
FIG 21 WOOD WHEEL SILK PLATINUM PARAFFIN ADMITTED AT POINT P
FIG 22
WOOD WHEEL PARAFFIN SILK PLATINUM
PARAFFIN ADMITTED AT P
NORMAL TEMPERATURE FROM + TO 0
FIG 23
COPPER WHEEL SILK PLATINUM
PARAFFIN OIL ADMITTED AT PT P
FIG 24 WOODEN WHEEL SILK THERMOPILE PLATINUM
A = AMMETER E = ELECTROMETER
AMMETER READINGS
FIG 25 WOODEN WHEEL SILK PLATINUM THERMOPILE
CURVE E ELECTROMETER
CURVE A AMMETER

The experiment with the paraffin oil and wooden wheel was now varied by *heating* the oil. For this purpose a coil of lead piping was placed in the vessel, through which steam could be blown. The result is shown in fig. 22. The oil was admitted at the ordinary temperature 10° C. at P, and after a fall of potential the steam was turned on at the point +.

The potential then began to rise and continued to rise until the temperature of the oil reached 75° C.

The potential then remained fairly constant until the temperature rose further to 90° C. At this temperature the potential fell suddenly, apparently due to the insulation of

the oil breaking down (see tests on paraffin later). The current of steam was then cut off and when the temperature had fallen to about 70° C. the potential began to rise again, indicating a recovery of the insulating power of the oil.

This apparent breaking down of the insulation of oil as the temperature increased was observed on many occasions when this experiment was repeated *.

With the copper–silk wheel the result is shown in fig. 23. In air the potential quickly reached a high steady value, and the introduction of the pure paraffin at P causes a fall which, however, later gives place to a rise, continuing to the end of the experiment. It seems probable that in this experiment (as in those made with the wood and slate wheels in paraffin oil) the charge on the wheel escapes through the axle, and that in the later stages of the experiment the oil itsel becomes charged with electricity of the same kind as that on the specimen. This might account for the rise of potential towards the end of these experiments.

### *Tests on Paraffin Oils.*

#### *Lamp-Oil.*

A glass vessel was taken and half filled with crude paraffin oil, the mouth of the jar being fitted with an ebonite stopper, through which passed two brass rods dipping into the oil. One rod was earthed and the other connected to an electroscope ; the latter was charged by means of an ebonite rod and flannel in the usual way, but the leaves collapsed quickly. The experiment was done several times, but with the same result. When there was no paraffin oil in the vessel the electroscope, when charged, remained charged. Hence the conclusion arrived at was that crude paraffin oil was not an insulator.

#### *Pure Paraffin Oil.*

The same kind of experiment as the one above was carried out with pure paraffin oil. The electroscope was charged as before, the leaves collapsed, but this time much slower. Pure paraffin oil is a much better insulator than the lamp-oil, but nevertheless there was a natural leakage through it.

This experiment was carried to a further stage. The temperature of the oil was raised from normal to 100° C. As the temperature went up (the electroscope being charged

* In fig. 22 the marked drop of potential at the 30th minute was probably accidental.

at frequent intervals during this period) it was noticed that the leaves collapsed more quickly, until it became impossible to keep a charge on the electroscope. The oil was then allowed to cool, and as it did so the leaves of the electroscope took longer to fall. From these experiments it would seem that the insulating power of paraffin oil depends on its temperature.

*Variation of the Temperature of the Specimen during Friction.*

The following experiment was made for the purpose of observing the change of temperature of the specimen, as well as its change of potential, during the friction.

The platinum was mounted on the outside of a brass cup which served as a cover for a thermopile consisting of antimony and bismuth elements. The thermopile was supported on the ebonite arm E (fig. 1) and was therefore immediately behind the specimen during the friction experiment. Insulated connecting-wires led from the thermopile to an ammeter, which was also insulated. Simultaneous readings could thus be taken of the potential and temperature variation of the specimen, the latter being proportional to the ammeter readings.

The results of two experiments of this kind are shown in figs. 24 and 25, the wood–silk wheel being used in each case. It will be seen that except in the early stages of the experiment the rise of temperature is nearly proportional to the rise of potential, the two curves running nearly parallel to each other. These experiments seem to indicate that there is some connexion between the temperature of the rubbing-surface and the amount of frictional electricity produced.

*Frictional Electricity and Contact Electricity.*

An experiment was made with an object of examining whether any appreciable amount of electricity could be produced on the platinum specimen by bringing it into contact with the silk under high pressure. According to v. Helmholtz, frictional electricity is merely contact electricity, the effects of the friction being only to bring the surfaces into clear contact. On the other hand, both M. Owen and Morris Jones, in the papers referred to, found that no charge was produced on their specimens by pressure alone. The pressures used in their experiments were, however, not very great, and it was therefore thought desirable to repeat the experiment with much greater pressure.

Accordingly the platinum disk (still connected to the electrometer) and a piece of new silk were placed between the jaws of a vice, being well insulated from them by thick pieces of ebonite. The electrometer reading was taken first without pressure on the specimen, then when the vice was tightened up as much as possible. The experiment was repeated several times, but in no case was the electrometer deflexion due to the pressure as great as 1 cm. Repeating the friction experiment immediately afterwards, with silk-covered wheel and platinum disk, the deflexion at once rose to over 20 cm. This experiment therefore confirms the observation of Owen and Morris Jones that contact electricity and frictional electricity are phenomena of different orders of magnitude.

## *Summary.*

The results arrived at in this paper may be summarised as follows :—

(1) When electricity is produced on a metal by friction with silk the amount produced depends greatly upon the material used as a basis for the silk ; to ensure a large amount of electricity the material should not be an insulator, but should possess an appreciable degree of conductivity.

(2) If a metal is rubbed for a prolonged period with silk, the potential of the metal undergoes fluctuations, which may be due to the silk being rubbed away in layers or to a fatigue of this material similar to that which has previously been observed in ebonite.

(3) If a metal is being rubbed by silk in air, and if the potential of the metal is low, the introduction of any one of the following gases, coal-gas, hydrogen, carbon dioxide, to replace the air, causes the potential to rise. On the other hand, if the potential in air was high, the admission of one of these gases caused the potential to fall.

(4) The introduction of sulphur dioxide to replace the air in all cases caused the potential to rise, whether the potential in air was high or low. How far this effect may be due to the superior conductivity of this gas has not yet been determined.

(5) Oxygen, and still more ozone, always caused a fall of potential as compared with that developed in air. This effect does not appear to be due to leakage through these gases. It is suggested that the fall of potential in oxygen may be due to a partial ozonization of the gas by the field, due to the frictional electricity.

(6) The influence of these gases on the amount of frictional electricity produced is greatest when the silk-rubber is mounted on a metal basis.

(7) If the air surrounding the rubbing-surfaces is replaced by a liquid medium, the potential of the metal is higher if the liquid possesses appreciable conductivity; ordinary lamp-oil is superior in this respect to pure paraffin. This effect may be partly due to the removal by the liquid of some of the charge on the silk rubber, as suggested in the case of $SO_2$.

(8) The effect of a liquid insulator (*e.g.* paraffin oil) as medium increases with rise of temperature of the liquid up to a certain point. This may be due to the gradual increase of conductivity of the liquid. At a certain temperature, however, the insulation of the oil appears to break down, and the production of frictional electricity almost stops.

(9) The temperature of the rubbed metal surfaces rises almost in proportion to its potential.

(10) The metal wheel gives the best result in *air*, ebonite the poorest. While the ebonite wheel gives the best result in oil, metal the poorest.

(11) The order of the gaseous media for the best production of frictional electricity :—

1. Sulphur dioxide.
2. Air.
3. Nitrogen.
4. Coal-gas.
5. Hydrogen.
6. Carbon dioxide.
7. Oxygen.
8. Ozone.

*Liquid Media.*

Crude Lamp-Oil.
Pure Paraffin.

---

## CXXVII. *Notices respecting New Books.*

*The Theory of Measurements.* By L. Tuttle and J. Satterly. (Longmans, Green & Co., 1925. Price 12*s.* 6*d.* net.)

THIS book is intended to furnish an introduction to some of the applications of the exact sciences and their relation to the practical sciences and useful arts, and also to emphasize general considerations of measurement, theory of errors, general methods of procedure, quantitative accuracy, adjustment of observations, and so on. It presupposes very little mathematical equipment in the student, and is written in such a way that it can be read with profit at school or in the first year at the University.

It is also possible that this book may prove very helpful to the

student of scientific method. For it deals in a simple and direct way with many of the processes in everyday use in all sciences; and it would open the eyes of the professional logician who studies traditional logic to go through this book chapter by chapter and give an analysis of the logical processes used.

We congratulate the authors on producing a most useful introduction to a large number of topics which are of methodological, and also of general scientific interest. The book should certainly be recommended to the elementary student, who, after its careful perusal, should be ready to tackle such a treatise as Whittaker and Robinson's 'Calculus of Observations.'

D. M. W.

*A Practical Treatise on Fourier's Theorem and Harmonic Analysis for Physicists and Engineers.* By A. Eagle, B.Sc. (Longmans, Green & Co., 1925. Price 9*s.* net.)

This book should certainly make a wide appeal to the public for which it is written. It is always a difficult matter to decide exactly where the line should be drawn when a piece of mathematics is being taught to students whose only concern with the subject is in applying the results already well known. And it is especially hard to make this decision in Fourier analysis.

There are various features of the book which make it of considerable value. First of all, the Preface (*mirabile dictu*) actually attempts to give a bird's-eye view of the territory to be studied. And this is done so successfully that an intelligent student should be able to appreciate the nature of Fourier's theorem and its place in mathematical analysis fairly adequately at the outset. In many text-books so much attention is given to the mathematical details of the investigations, that the average student—or even the moderately intelligent student—may have no idea whatever of the dominating idea in the part of mathematics which he has been studying, even though he may be able to attain to a modest competence in the working of specific problems belonging to the subject. There should be little danger of this in the present case if the preface is intelligently read.

There is an introductory chapter on imaginary quantities, which in itself is interesting and fairly adequate. It is a severe indictment of the teaching of physicists and engineers if it is really necessary to include it in the present work. When we reflect on the fact that the theory of complex numbers presents one of the most convenient illustrations of the methods used in mathematical definitions, it is quite extraordinary that those responsible for introducing elementary students to mathematics omit it—if indeed they do omit it—from their courses.

The introduction and discussion of Fourier's theorem and of periodic functions is accompanied by a number of illustrations drawn from subjects of which the student presumably already has some knowledge. And this is another good feature of the

book. For in this way the student is encouraged to understand why Fourier analysis is of fundamental importance before he tries his hand at the mathematical details which may divert his attention when he comes to make applications for himself.

The next chapter deals with theoretical considerations. And here the student will find a discussion of a number of important considerations relating to the convergence of series and integrals, and the properties of functions relevant to their expression as Fourier series and as integrals. Finally, there is a chapter on Fourier's Integral Theorem to which is appended (as in the earlier chapters) useful examples and problems.

The following chapter is concerned with the search for periodicities in observed data which are not periodic.

Finally, there is a short historical survey of the subject, which is calculated to increase the attractiveness of the book.

D. M. W.

*The Dynamical Theory of Sound.* By H. Lamb, F.R.S. Second Edition. (Arnold & Co., 1925. Price 18*s.* net.)

We welcome the new edition of this valuable text-book which has just been issued. Professor Lamb has for a long time now provided the outstanding example of the brilliant mathematician, who combines research of the most fundamental importance with the deepest interest in the teaching of his subject. And it is difficult to know how he has managed to find time to take the pre-eminent position which is his in these two very different domains of research and teaching. For some generations to come both the humblest and the most advanced student of mathematical physics will owe him a debt of gratitude, and it is to be hoped that Professor Lamb is fully conscious of the deep appreciation of the present generation of students and research workers of his splendid labours in the cause of mathematical education.

The present work provides an introduction to the mathematical theory of Sound. It contains the general theory of Vibrations, and the application of these investigations to Strings, Bars, Membranes, and Plates. Incidentally there is a chapter which provides an introduction to Fourier's Theorem. This chapter was a necessary part of the book when it was first issued. However, nowadays, more attention is given, even in elementary courses, to such fundamental theorems of analysis, and there will probably be few students who will come to Professor Lamb's book in complete ignorance of Fourier's Theorem. The next chapters deal respectively with plane-waves of sound and the general theory of sound-waves. Then there is a discussion of simple-harmonic waves, and of various problems in which the scattering of sound-waves by an obstacle or through an aperture is under consideration. Next pipes and resonators are discussed, and among the references to recent applications of the subject which

have been added to this new edition is the reference in this section to Fage's analysis of the various periods of vibration of an airscrew by means of the selective hot wire microphone. An important chapter on Physiological Acoustics concludes the treatise. D. M. W.

---

## CXXVIII. *Proceedings of Learned Societies.*

### GEOLOGICAL SOCIETY.

[Continued from p. 888.]

February 25th, 1925 (*continued*).—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

THE following communication was read :—

'The Dissection of Pitching Folds.' By Prof. Arthur Hubert Cox, D.Sc., Ph.D., F.G.S.

The dissection of a pitching fold may, under certain conditions, so affect outcrops that the true nature of the fold may be more or less completely obscured, so that in extreme cases an anticline may easily be misinterpreted as a syncline, and *vice versa*. In a pitching anticline cut along a plane inclined in the same direction as the fold-axis, but at a smaller angle, the outcrops form a curve closing towards the pitch. If the inclination of the plane of dissection is fairly steep, as on a mountain-side, the effect is that the outcrop-curve sags downwards towards the centre of the fold-axis, giving a false impression of a syncline. An example of such a structure on Cader Idris is figured and described.

By altering the inclination of the plane of dissection across a pitching fold, outcrops can be made to take any desired curve, either concave or convex. In a pitching anticline the curves will have a downward convexity when the inclination of the dissecting plane is less than the angle of pitch, but an upward one when the direction of inclination of the dissecting plane is opposed to that of the pitch. There must, therefore, be some intermediate position in which the outcrop 'curve' is such that its projection on the map appears as a straight line, and the outcrop crosses the fold without apparent deflection.

A two-dimensional projection of a three-dimensional structure may be quite misleading. In some cases, the elevation, or the nearly vertical projection, like the view of a mountain-side, will be deceptive; in other cases, the geological map representing the horizontal projection will be deceptive. Such deceptive projections are liable to occur in districts of high relief, and may account for some of the difficulties experienced in tracing the continuity of folds across such areas.

---

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]